Stability of polyelectrolyte multilayer micropatterns in response to post-treatments

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A R T I C L E   I N F O
Article history:
Received 5 September 2011
Received in revised form
14 December 2011
Accepted 4 January 2012
Available online 12 January 2012

Keywords:
Compression
Patterns
Multilayers
Polyelectrolytes
Post-treatment

A B S T R A C T
Post-treatments of the micro-molded poly(4-styrenesulfonic acid-co-maleic acid, 1:1 SS:MA) sodium salt (PSSMA)/poly(diallyldimethylammonium chloride) (PDADMAC) multilayers in water or at elevated temperature were conducted to disclose the stability and transformation of patterns prepared at different conditions. The compression induced patterns kept unchanged regardless of the incubation time, while the lateral flow induced patterns disappeared rapidly within 10 min in water. Results showed that the pattern disappearance was not caused by the remodeling or swelling of the multilayers, but caused by mass loss of the uncompressed region. Heat treatment of the high ridge patterns could greatly decrease their height and stabilize the pattern structure. The double strip patterns could be transformed to the high ridge patterns and the linear patterns by annealing at 70 °C for 3 h and 6 h, respectively. Therefore, the pattern features and stability against water etching can be effectively modulated by the post-treatment time at elevated temperature.

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1. Introduction

Micropatterning on multilayers can endow the ultrathin film with regular geometric physical or chemical structures, and thereby broaden their potential applications in electronic, medical and other advanced technological fields. So far several methods such as micro-contact printing, nano-imprint, compression etc. have been developed to micropattern the multilayers [1–6]. The multilayer compression is easily handled at very mild conditions without involvement of expensive machines. Previous results show that many factors can influence the compression behavior, such as multilayer compositions, environmental humidity, drying time and salt treatment [6–10].

More recently, poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA), which contains both strong (sulfonate) and weak (carboxylate) charging units, is used to prepare the multilayers [10–12]. Compression of these multilayers dried at 70% relative humidity and room temperature for 2 h, 6 h and 12 h by a poly(dimethyl siloxane) (PDMS) stamp with linear features obtains double strips, high ridges and linear patterns on the multilayers, respectively [10]. Compression of the PSSMA/PDADMAC multilayers is also greatly affected by the types of salts used during the multilayer assembly [11]. At pH 4, the multilayers are much easier compressed, which in turn reduces significantly the synthesis of Ag nanoparticles in the multilayers [12]. The polyelectrolyte multilayers are held together by the ionic bonds, which may break and re-form in solution and thereby enable the remodeling of the multilayers toward the lowest energy state. This would mean that the patterns formed under the external force at different drying time might behave different alteration when they are re-incubated in medium like water. Indeed, of the various factors influencing the pattern formation, the drying time is the most efficient one that not only results in the huge variation of the pattern height and features but also the difference in mechanism of pattern formation. For example, the regular patterns at a longer drying time are obtained by vertical compression of the multilayers (compression-induced patterns), while the high ridges or double strips at a shorter drying time are resulted from lateral flow of the multilayers during the compression (lateral flow-induced patterns) [10]. Preliminary observation showed that the high ridges disappeared after incubation in water for 5 h, while the compression-induced patterns kept unchanged [10]. However, the kinetics of the alteration, i.e. the time required for the pattern disappearance, is not known. It is not known either if it is caused by a simple recovery of structure or/and erasure of the high ridges. Furthermore, since the stability of the patterns should be taken into consideration in a great priority for almost all the potential applications, it is necessary to explore efficient method for stabilizing the lateral flow-induced patterns.

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doi:10.1016/j.colsurfa.2012.01.013
In this paper, attention shall be paid to the post-treatments of the pattern compressed PSSMA/PDADMAC multilayers in water or at elevated temperature. Particularly, the alteration kinetics of the pattern compressed films dried for 12 h or 6 h shall be elucidated as a function of post treatment time in water. Measures are also taken to stabilize the pattern structures by annealing at higher temperature. Physical insights during these alteration processes shall be discussed too.

2. Experimental

2.1. Materials

Polyethyleneimine (PEI, Mn 60 kDa, Mw 750 kDa), poly(diallyldimethylammonium chloride) (PDADMAC, very low molecular weight) and poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA, SS:MA 1:1, Mw 20 kDa,) were obtained from Aldrich and used as received to prepare 1 mg/mL/1 M NaCl solutions, respectively. Poly(dimethylsiloxane) (PDMS) pre-polymers, Sylgard 184, were obtained from Dow Corning and were used to fabricate the PDMS stamps with desired pattern structures.

2.2. Substrate preparation

Silicon wafers and quartz slides were firstly cleaned with Piranha solution (70:30, v/v% sulfuric acid/hydrogen peroxide) (Caution: piranha is a strong oxidizer and should not be stored in a closed container), and then were sonicated in a 1:1 mixture of water and 2-propanol for 15 min. They were further treated in a 5:1:1 mixture of water, hydrogen peroxide (30%) and ammonia solution (29%) at 60 °C for 15 min. After the wafers were rinsed in copious amount of water, they were blown dried with a nitrogen stream.

2.3. Assembly of polyelectrolyte multilayers

To establish a highly charged precursory layer on the surface, a layer of PEI was firstly deposited on the silicon and quartz substrates. Sequential adsorption of the polyelectrolytes on the silicon and quartz substrates was then performed by manually dipping. Between alternate exposures to two kinds of polymer solutions for 15 min, there were 3 rinses with triple-distilled water for 3 min. After the desired layer numbers were deposited, the PSSMA/PDADMAC multilayers were rinsed with triple-distilled water for at least 5 min to eliminate the adsorbed salt. The multilayers were then dried in 70% relative humidity (RH) at room temperature (20 °C) for desired time.

2.4. Creation of the patterns under pressure

The PDMS stamps with strips were molded from lithographically prepared masters [13,14]. The soft PDMS stamps were put onto the polyelectrolyte multilayers with the patterned surfaces toward the multilayers under a normalized pressure of 200 g cm⁻² at room temperature in 70% RH. Two hours later, the stamps were carefully peeled off to obtain the patterned multilayers.

Fig. 1. (a and c) Pattern height on PEE/PSSMA/PDADMAC multilayers as a function of post-treatment time in water at room temperature. The patterns were made after the multilayers were dried for (a) 12 h and (c) 6 h, respectively. Insets are representative SFM images measured at the post-treatment time indicated by the arrows. (b and d) UV-vis spectra of original, pattern compressed and post-treated multilayers which were initially dried for (b) 12 h and (d) 6 h, respectively.
2.5. Post-treatment of the patterned multilayers

The PSSMA/PDADMAC multilayers typically dried for 6 and 12 h in 70% RH at room temperature and patterned with the PDMS stamps were incubated in water at room temperature for different time. In the annealing treatment, the patterned multilayers were incubated in air at 70 °C for 3 h or 6 h in an oven. The remained height and surface morphology of the patterned multilayers was then checked by scanning force microscopy (SFM).

2.6. SFM

Topographical images were collected using a SFM from Seiko Instruments Inc., Japan (SPI3800N Probe Station and SPA400 SPM Unit) in a dynamic force mode. Silicon tips with a resonance frequency \( f_0 \) of 150 kHz and a spring constant of 20 N/m were utilized. The scanning frequency was 0.5 Hz. The contact force between the tip and the samples was kept as low as possible (<2.5 nN). To measure the film thickness, part of the films was scratched off by a thin needle of syringe. Then the height difference between the exposed silicon substrate and the multilayers was measured.

2.7. Ellipsometry

The thicknesses of the multilayers (30–60% relative humidity) were also measured by ellipsometry. The measurement was carried on a variable-angle spectroscopic ellipsometer (model M2000D; J.A. Woollam Inc., Lincoln, NE) at incident angles of 65°, 70°, and 75° within a wavelength range of 600–1700 nm. The thickness was calculated from the ellipsometric parameters, \( \Delta \) and \( \psi \), by which the film thickness and refractive index was automatically fitted using a Cauchy model. Data were obtained on different place of the film and reported as mean ± standard deviation.

2.8. UV–vis spectroscopy

The UV–vis spectroscopy of the multilayers prepared on quartz substrates was obtained by a UV–visible spectrophotometer, UV-2450, Shimadzu.

3. Results and discussion

To study the influence of post-treatments on the multilayer stability, the PEI(PSSMA/PDADMAC)\(_7\) multilayers were assembled in 1 M NaCl. They had a thickness of \( \approx 42 \) nm characterized by SFM and ellipsometry. The variance between these two methods was within 1 nm. The film was then typically dried for 12 h or 6 h in 70% RH before it was pattern molded with a PDMS stamp having a physical pattern structure of strips (6 \( \mu \)m \( \times \) 6 \( \mu \)m in width and space with deepness of 2 \( \mu \)m). The linear patterns made at these two conditions have an average height (the difference between the compressed area and uncompressed area) of 35 nm and 105 nm as shown in the insets of Fig. 1a and c at the 0 time point, respectively. Fig. 1a shows that the compression-induced patterns kept their features and height without detectable changes within a 12 h post-treatment in water, revealing that they are not influenced by post-incubation regardless of the time. By contrast, the lateral flow-induced high ridge patterns were instantaneously lowered from 105 nm to 8 nm upon treatment in water for only 10 min, and then slowly decreased until 12 h, at which the patterns was...
remained only about several nanometers and could be hardly observed (Fig. 1c). It is worth mentioning that the lateral flow-induced double stripe patterns at 2 h also could be rapidly erased when they were treated in water (data not shown). The results imply that the lateral flow-induced patterns disappear with a very fast rate, e.g. less than 10 min.

The disappearance of the multilayers can be either resulted from the mass loss or the remodeling of the multilayers or the both. To clarify this point, the multilayers after compression and post-treatment in water for 12 h (Fig. 1b) or 6 h (Fig. 1d) were compared with the pristine ones by UV–vis spectroscopy. Fig. 1b shows that the absorbance of styrene sulfonate group at 225 nm was not changed regardless of the compression and post treatment, confirming no mass loss. By contrast, apparent mass loss was found after the lateral flow-induced patterns were incubated in water for 5 h, but the compression alone did not bring change of the absorbance at 225 nm (Fig. 1d). Since both the mass and structure of the compression-induced patterns kept unchanged, next our focus shall be paid to the lateral flow-induced patterns in terms of structure variation and improvement of stability.

To explore the structure change in detail of the lateral flow-induced patterns, part of the multilayers was scratched off with a thin needle of syringe along the perpendicular direction of the linear patterns. Before treatment in water, the pattern height was about 100 nm (Fig. 2a, the red line). The total height of the patterns (the height difference between uncompressed area of the multilayers and silicon substrate) was about 115 nm (the blue line), which equals exactly the pattern height (100 nm) and the height (15 nm) of the compressed region (the height difference between compressed area of the multilayers and silicon substrate) represented by the black line (Fig. 2b). After being incubated in water for 5 h (Fig. 2c), the net pattern height decreased from ~100 nm to 5–9 nm which is consistent with the result of Fig. 1c. Correspondingly, the total pattern height was decreased from 42 nm (the pristine multilayers) to 23 nm. However, the height of the compressed region kept unchanged (15 nm) (Fig. 2d). These values matched very well with each other, confirming the alteration of the pattern structures.

In this type of patterns, the compressed region is very stable and does not change during the incubation in water. However, the uncompressed region, i.e. the formed patterns, is not stable and can be easily erased, leading to the huge decrease of the pattern height. Although the remodeling of the patterns can not be completely ruled out at present, the pattern height decrease is definitely not caused by the swelling of the compressed area of the multilayers and thereby the reduction of the height difference between the compressed and uncompressed regions. A simple calculation knows that the volume decrease of the compressed region is $(42–15)\times f$ nm $\times$ feature area, while the volume increase of the patterns is $f \times (100–42)\times$ feature area. The feature area is same for the compressed region and the uncompressed region, thus the volume ratio equals $f \times (100–42)/(42–15)=2.15f$. Considering the real shape of the ridges in cross-section is between the trapezium and trapézium, the factor $f$ should be larger than 0.5. Therefore, an overall expansion of the multilayer volume must have occurred, resulting in a lower density of the uncompressed region. Moreover, macroscopic physical defects may be formed simultaneously. All of these changes are responsible for the mass loss of the lateral induced patterns.

Now that the lateral flow-induced patterns are easily erased, measures must be taken to stabilize the patterns. It is well known that elevated temperature can promote the relaxation and confirmation re-adjustment of polymer chains as well as the healing of physical defects. As shown in Fig. 3, after the lateral flow-induced patterns (Fig. 3a) were treated at 70°C for 3 h, their height was...
decreased sharply from ∼100 nm to ∼40 nm (Fig. 3b). The annealed patterns showed a significantly improved stability, e.g. the patterns kept their topology with a slight decrease of their height from ∼40 nm to ∼30 nm after incubated in water for 2 h (Fig. 3c).

The annealing could also make the transformation of the pattern topography, for example, from double strips obtained on the PEI(PSSMA/PDADMAC)_7 multilayers dried for 2 h to the high ridges as shown in Fig. 4. The double strips had a height of 65–85 nm (Fig. 4a) and could be similarly erased. After treated at 70 °C for 3 h in oven, they changed to high ridges with a height of 60–70 nm (Fig. 4b). Apparently, the high ridges should be built up from the double strips as a result of flow of the softened multilayers at a high temperature. Indeed, some unfilled voids in the middle of the ridges were still remained, which are indicative of the building up format of the ridges, i.e., from the boundaries to the middles. However, with this structure the transformed patterns were still unstable. A further treatment at 70 °C for another 3 h (totally 6 h) yielded the patterns with a height of 25–33 nm (Fig. 4c), which was lower than the pristine multilayers. At this state, the multilayers were fully re-adjusted and were stable against water treatment.

pristine multilayers, and show good stability against water treatment. A 6 h drying at 70% RH, however, results in high ridges which are formed by lateral flow of the multilayers from the uncontacting regions of the PDMS stamp (Fig. 5b). They are not stable in water and can be erased accompanying with large mass loss. Heat treatment at 70 °C for 3 h decreases the ridge height to a degree which is comparable with that of the compressed patterns (12 h drying), and also stabilizes the patterns against water treatment (from Fig. 5b to a). Micro-molding on the 2 h dried multilayers yields double strips (Fig. 5c), which can be erased in water, but can be transformed to the state of ridges by 3 h treatment at 70 °C (from Fig. 5c to b). Treatment at 70 °C for 6 h transforms the double strips to the patterns which are comparable with those directly obtained on the 12 h dried multilayers (from Fig. 5c to a). Therefore, by applying the post annealing on the lateral induced patterns, the pattern features and stability against water etching can be effectively modulated.

4. Conclusions

We explored in this work the kinetics stability and post-treatments of the compression and lateral flow-induced patterns on the PSSMA/PDADMAC multilayers assembled in 1 M NaCl solution, respectively. The pattern height decreasing in water is not caused by the swelling of the compressed area of the multilayers but caused by erosion of the uncompressed region. Molding on the PEI(PSSMA/PDADMAC)_7 multilayers dried at 70% RH for 12 h creates vertically compressed patterns with neglectable lateral flow, if any (Fig. 5a). These patterns have a thickness smaller than their
Acknowledgments

This study is financially supported by the Natural Science Foundation of China (20934003), and the Major State Basic Research Program of China (2011CB606203).

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