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Study of leading factors in formation of surface wavy structures on a rubber material

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Abstract

Wavy structures are often observed on the surface of a rubber material (polydimethylsiloxane, PDMS) covered with a thin metallic film. In this study we demonstrate that the orientation, periodicity, location of formation, and range of periodicity of the wavy structures can be regulated by three leading factors including the surface pattern, substrate hardness and the thickness of the metallic film. Results show the orientation of the wavy structures can be adjusted by the location, shape and size of the surface patterns. Enhancement of the substrate hardness can prevent forming random wavy structures. The thickness of surface metallic film significantly influenced the periodicity of the structures. Experimental results revealed an increase of the thickness of surface Au film by 50 nm, the periodicity was increased roughly by 1 μm. A compound structure, combining longitudinally preset patterns and transversely induced wavy structures, and a parallel wavy structure fabricated, respectively, by suitable arrangement of pattern configurations and adjustment of substrate hardness were demonstrated. The relatively simple approaches proposed here show the potential application in fabrication of designated complicate structures.

Keywords: PDMS; Wavy structure; Grating

1. Introduction

A large-area and ordered wavy surface structure is of fundamental interests and also with practical importance in areas, such as microelectromechanical systems (MEMS), micro-optics, biology, and micro-fabrication [1]. A more straightforward method for formation of wavy structures on a PDMS surface was first presented by K. Burton et al. in 1998. They reported that the ordered waves, with wavelengths between 20 and 50 μm, were formed on a PDMS surface that had been patterned in bas-relief [2]. Their method was accomplished by heating a patterned polydimethylsiloxane (PDMS) substrate on which a 5 nm-thick titanium layer was pre-coated as an underlayer and over the underlayer was covered with a gold film with thickness of 50 nm. In order to reduce the periodicity or to control orientation of the wavy structures, different surface treatments on rubbery materials, involving plasma oxidation, deposition of multiplayer metals, and introduction of compressive stress by special machines [3–6], have been proposed. These methods have demonstrated that the periodicity and orientation of the wavy structures can be effectively controlled. However, low-cost methods for generating well-controlled and high-quality surface wavy structures are still very much expectable.

In this study, the periodicity and orientation of wavy structures are modified from three major effects: shape of the pattern on the PDMS substrate; hardness of the PDMS substrate; and, thickness of the surface metallic film. To understand the effect of the pattern shape on the wavy structures, convex patterns with both circular and square shapes and concave patterns with circle shapes were created on the PDMS substrate. Orientations of structures around a single pattern and among patterns in array were also presented and discussed. Effects of hardness of the PDMS substrate on the surface wavy structures were performed by adjusting the weight ratio of PDMS-Sylgard silicone elastomer to curing agent at the

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PDMS substrate preparing process. With changing the thickness of the deposited metallic film, the compressive stress, induced by different volumetric contraction rates between the metallic film and the PDMS substrate, could be varied that resulted in formations of different wavy structures.

This paper is organized as followed. After the introduction is the experimental section that presents the detailed processes for forming various surface wavy structures. The scanning electron microscope (SEM) images for surface structures formed at various fabrication conditions are shown in results and discussion section where possible mechanisms of structure formation and potential applications of these patterns are addressed. Major conclusions of this study are finally drawn in the conclusion section.

2. Experimental

Steps for fabrication of a PDMS substrate with desired patterns are described as following.

(1) The designed shape and size for the pattern on the PDMS substrate were first defined on a metallic mask through which the excimer laser wrote the pattern directly onto a polycarbonate (PC) plate. By monitoring the power intensity and number of laser shots, depth of the holes drilled by the excimer laser can be well controlled. The resultant PC plate with micro-holes that served as the master in the next step is shown in Fig. 1(a).

(2) The thermal curable liquid PDMS that mixed PDMS-Sylgard silicone elastomer and curing agent with the weight ratio of 10:1 was prepared. The liquid PDMS was poured onto the treated PC plate prepared from Step (1) and subsequently cured by baking it in an oven at 60 °C for 20 min. The solidified PDMS substrate with the desired pattern can be easily stripped from the master, due to its low surface energy. Fig. 1(b) shows the formation of the PDMS substrate with the desired patterns on the PC plate.

(3) A thin gold film with a reasonable thickness was then deposited on the surface of PDMS substrate, obtained up to Step (2), in a sputter. It was then cooled down rapidly to room temperature. Wavy surface structures were formed on the PDMS surface due to the different contraction rates of cooling between the Au film and the PDMS layer. The coefficients of thermal expansion of PDMS and Au are 960×10^{-6} and 14×10^{-6}/K, respectively. The large difference in volumetric contraction rates introduced a compressive stress on the PDMS surface and led to the wavy surface structures. The schematic is shown in Fig. 1(c).

(4) The process of fabrication a PDMS substrate with lens-like bumps on surface, based basically on the excimer laser micro-drilling and spin coating techniques [7], is described here. Following Step (1), a thin liquid poly (methyl methacrylate) (PMMA) film was then coated on the polycarbonate plate with holes, micro-drilled by the excimer laser, by spin coating. As the liquid PMMA was rapidly spreading out, due to its own weight and the solution viscosity, a film, suspended on the micro-holes and with special curvature, was formed on the micro-holes. The liquid film was then cured thermally by baking at 60 °C for 5 min and it then sticks fixedly on the micro-holes. Repeating Step (2), the PDMS substrate with lens-like bump patterns was formed. After deposition of the Au thin film, described in Step (3), the wavy structure could be also found on this patterned substrate. The schematic is shown in Fig. 1(d).

3. Results and discussion

Three leading factors, including shape of pattern on the substrate, hardness of the substrate and thickness of the deposited metallic film on the substrate that might affect the periodicity and orientation of wavy structures are discussed here.

3.1. Effect of pattern shape

Demonstrated on Fig. 2(a) was the SEM image for the surface of a flat PDMS substrate covered with a gold thin film with thickness of 100 nm. The wavy structures were formed randomly on the surface. These structures were driven by the unbalanced compressive stresses that were induced by the large difference in volumetric contraction rates between the PDMS

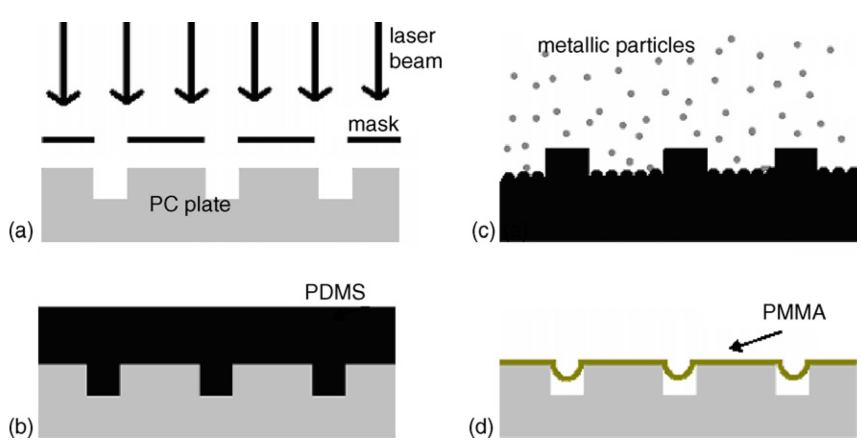

Fig. 1. Schematics showing the process of forming patterns and wavy structures on a PDMS substrate.

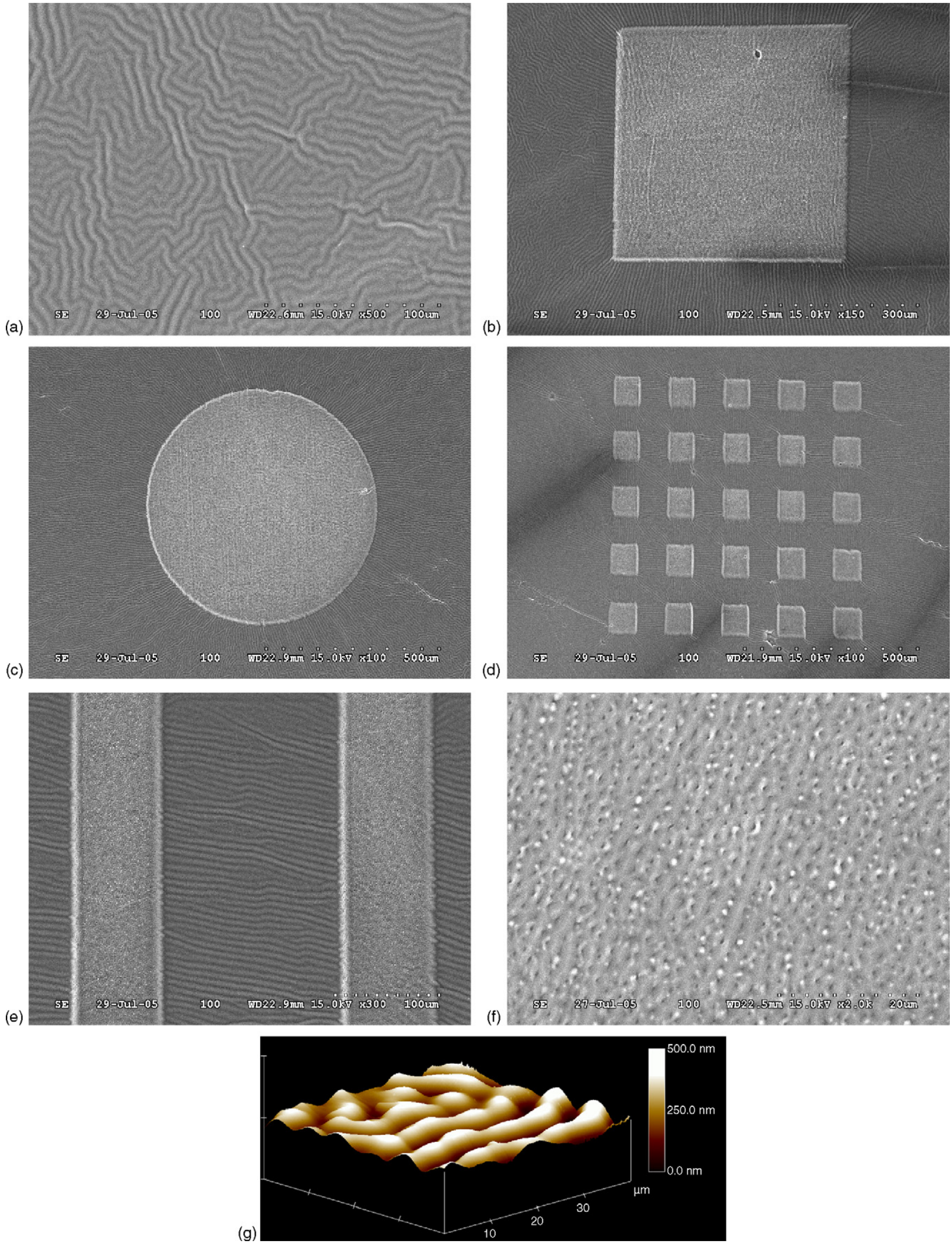

Fig. 2. (a–f) Showing the SEM images for the surface structures of the PDMS substrates covered with a thin gold film at different surface configurations: (a) on a flat substrate; (b) on a substrate with a square, step-like bumped pattern; (c) on a substrate with a circular, step-like bumped pattern; (d) on a substrate with 5 × 5 square, step-like bumped patterns; (e) a compound structures combing longitudinal slender patterns and transverse wavy structures; and (f) porous structures on the top surface of patterns; (g) the AFM image showing the surface topography for (a).

substrate and the Au film. Because there were no constraints on the PDMS surface, these unbalance compressive stresses led to the disordered wavy surface structures. The surface topography of these disordered wavy structures was shown in Fig. 2(g) that was scanned by an atomic force microscopy (AFM). The height of the wavy structure (distance from the crest to the trough, the peak-to-peak distance) was roughly within 500 nm.

To study the effect of the pattern on the orientation of the wavy substrates, a single step-like, bumped pattern was first examined. The corresponding surface wavy structures for a square pattern and a circle pattern were shown in Fig. 2(b and c), respectively. It was shown, instead of growing randomly, the wavy surface structures became more orderly close to the pattern. These ordered wavy structures stretched radically out from the boundaries of the pattern and were arranged in directions that were perpendicular to the sidewalls of the pattern. These ordered structures could, however, sustained only within a certain region close to the pattern boundary. Beyond that region, the random structures reappeared. The circular pattern shown in Fig. 2(c) was with a diameter of 750 μm and height of 10 μm. The range of the region for the ordered wavy surface structures in Fig. 2(c) was relatively larger than that in Fig. 2(b) where the square pattern was with side length of 450 μm and height of 10 μm. The heights for the wavy structures near to circular pattern and square pattern were about 4 and 2 μm, respectively. The range of the region for the ordered structures depended, on the other hand, more strongly upon the size of the pattern. With continuous increase of the pattern size, the constraint to the growth of the random wavy structures was enhanced that resulted in increasing both the range of the ordered region and the height of the wavy structure.

The wavy structures on the PDMS substrate with patterns in array were also considered. An array with 5×5 square patterns, each pattern having a side length of 100 μm, height of 10 μm, and pitch of 100 μm, was studied. According to the general rule for generating the surface wavy structure discussed in the previous paragraph, orientations of the surface wavy structures were affected by the nearby bumped patterns. The resultant SEM image is shown in Fig. 2(d). The structures in the middle of patterns presented certain orders. Two groups of structures were observed. The first group is for the structures between parallel sidewalls of any two adjacent patterns. Their orientations were perpendicular to the sidewalls and thus presented either in horizontal or vertical directions on the SEM image. The second group was for the structures in regions in the midst of any four closest patterns. Their orientations were roughly aligned in the diagonal direction on the image, from the up-left to the bottom-right. Based on these observations, a

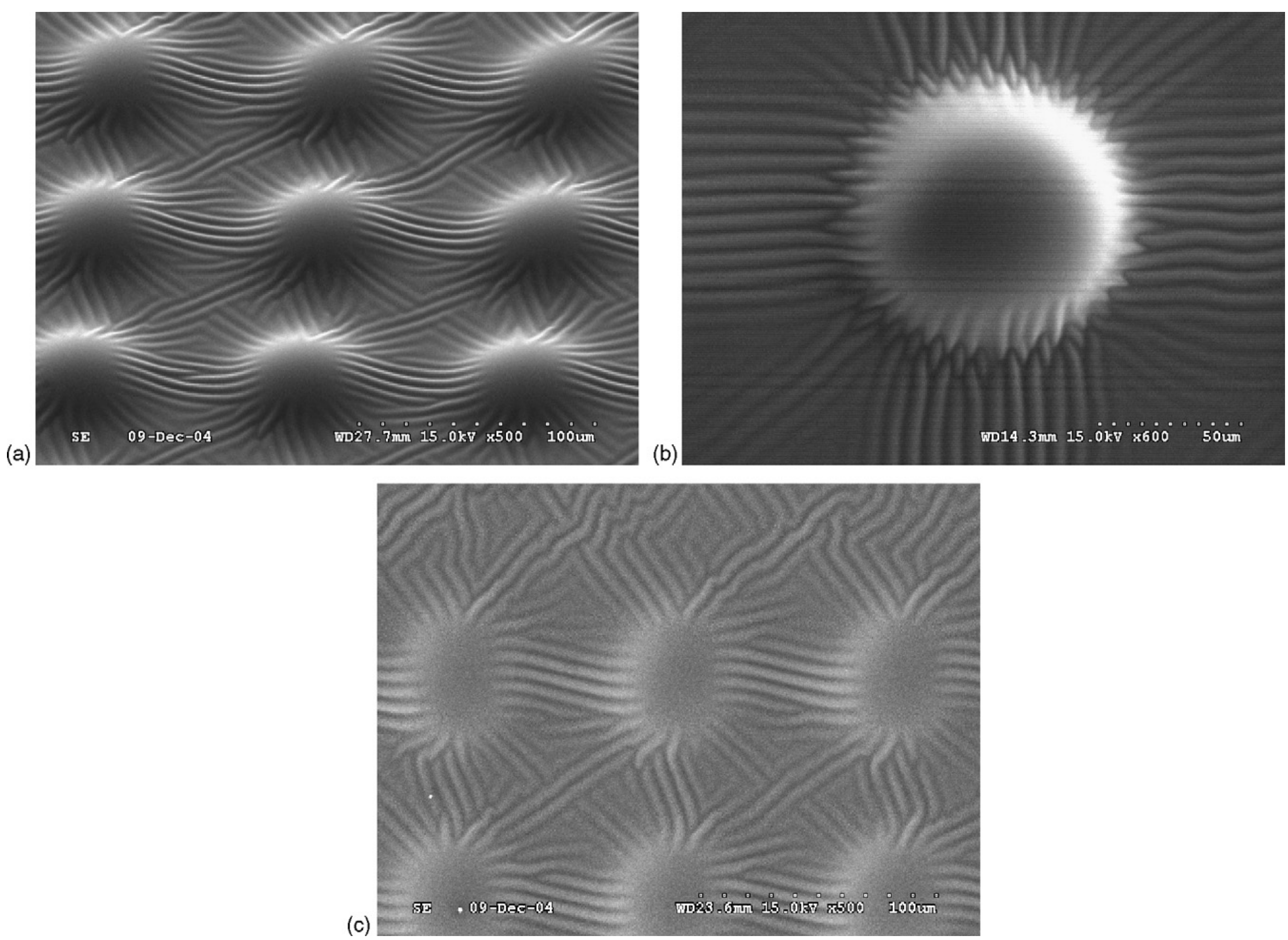

Fig. 3. SEM images showing the surface structures of the PDMS substrates covered with a thin gold film and having different surface patterns: (a) an array of 3×3 lens-like bumped patterns; (b) a single lens-like bumped patterns; and (c) an array of 3×2 circular, concaved patterns.

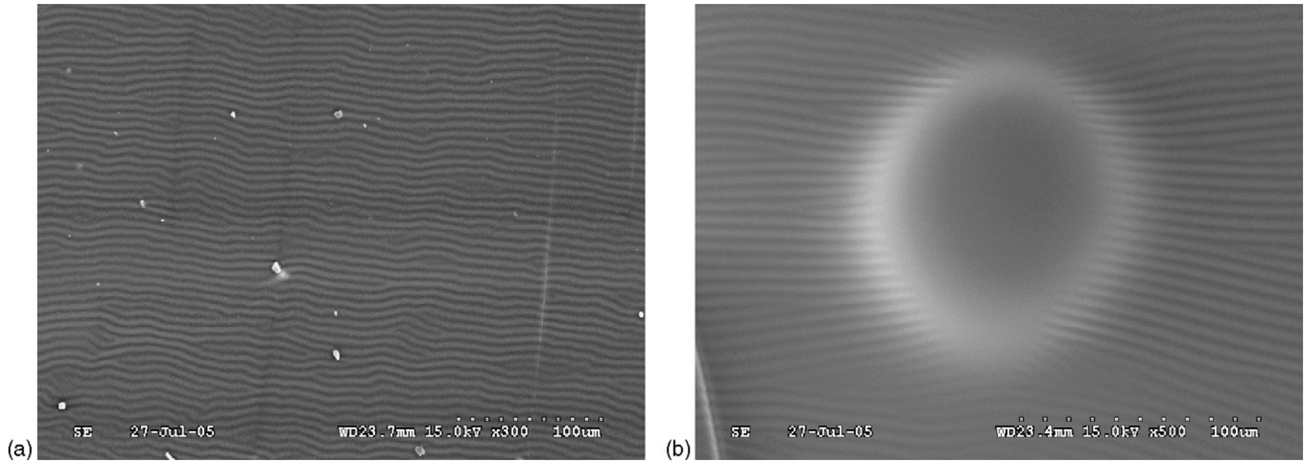

Fig. 4. SEM images showing the surface structures of the PDMS substrates with hardness-enhancement treatment. (a) On a flat substrate. (b) On a substrate with a lens-like bumped pattern.

compound grating, combining the vertical patterned grating and transverse wavy structures, could be fabricated by forming strip patterns on the PDMS substrate. The resultant SEM image for the wavy surface structures between two rectangular strip patterns is shown in Fig. 2(e). The width for each rectangular strip pattern was about 80 μm and the distance between the two strips was about 150 μm. The resulting periodicity of the wavy structures was about 4 μm. Finally, the structures on the top surface of a bumped pattern was also examined and shown in Fig. 2(f). Instead of the wavy structure, a porous structure, with pore size around 2 μm, was formed on the top surface of the bump pattern. It was conjectured that the rough exterior was

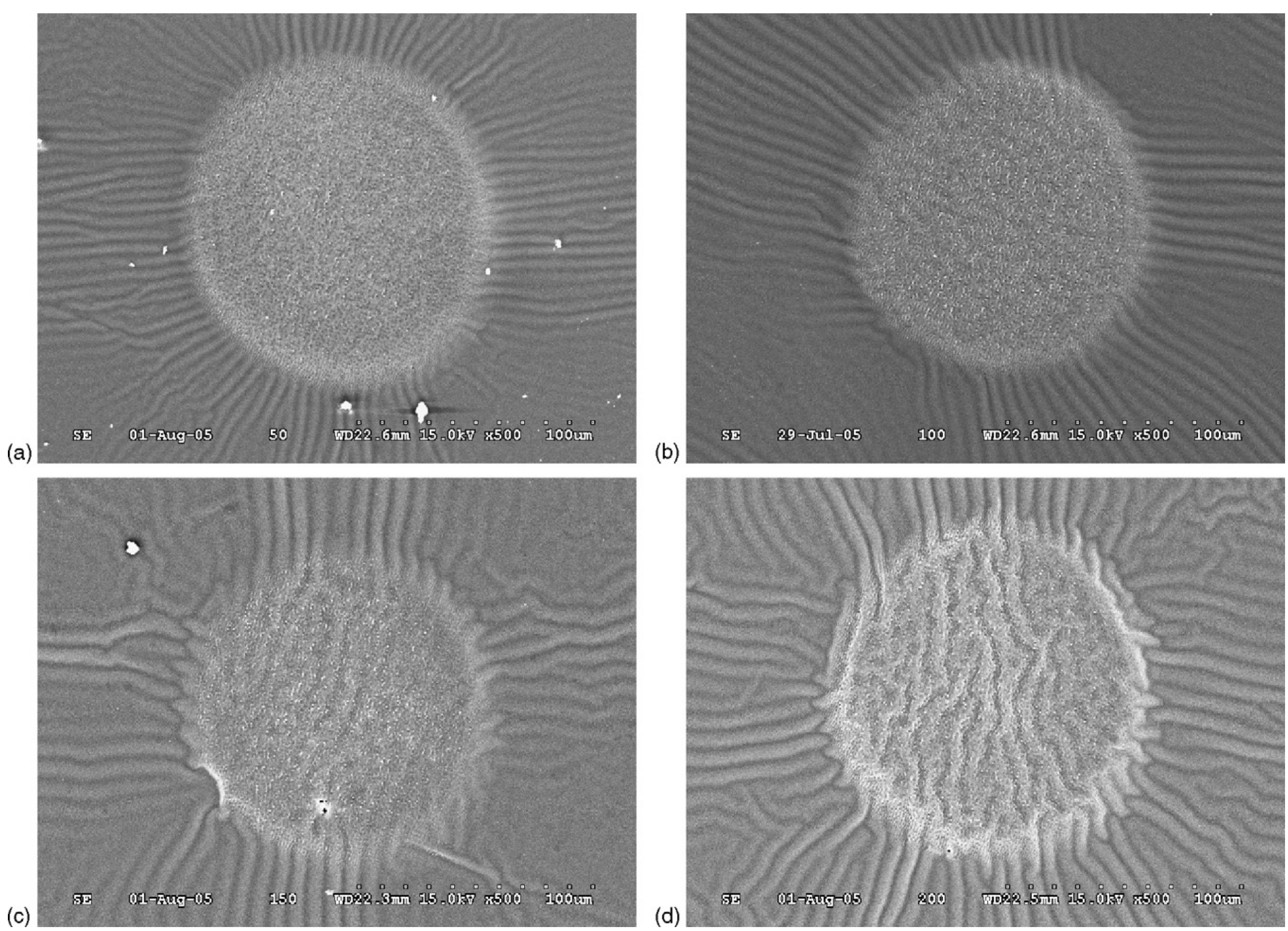

Fig. 5. SEM images showing the surface structures of the PDMS substrates with a circular, step-like bumped pattern covered with a gold thin film with different thicknesses. (a) 50 nm; (b) 100 nm; (c) 150 nm; and (d) 200 nm.

transformed from the PC plate through Step (2) where the unevenness was formed during the excimer laser micro-drilling process.

The PDMS substrate with patterns of lens-like bump was also discussed. Fig. 3(a) shows an array with 3 × 3 patterns. Each lens-like pattern was with a base diameter of 50 μm and height of 15 μm. Like the results presented in Fig. 2, the orientations of the wavy structures among patterns were affected by the existence of the patterns and showed particular regularities. The wavy structures close to the pattern boundaries, however, showed a different trend. In Fig. 2, they stopped at, or stretched out from, the pattern boundaries. In Fig. 3(a), they were, however, not bounded by the pattern boundaries and could extend, to some extent, to the surface of the patterns. This is because the boundary for the lens-like bumped pattern was relatively smooth and indistinct. The wavy structures could thus extend up onto the surfaces of the patterned regions. Fig. 3(b) shows the surface wavy structures around a single lens-like, circular bumped pattern that was with a base diameter of 100 μm and a height of 20 μm. Because the slope of the bump in Fig. 3(b) was steeper and the height of pattern was higher than those in Fig. 3(a), the extent of the wavy structures on the bump surface was relatively smaller. Hence, besides the slope, the height of the pattern affected the extent of the wavy structure propagating from the substrate onto the pattern surface.

In addition to the convex patterns, the wavy structures on the PDMS substrate with concave patterns were also examined. Fig. 3(c) shows distributions of the wavy structures on a PDMS substrate with an array of 2 × 3 concave circular patterns. Each pattern has a diameter of 50 μm. These concave patterns were formed by replica molding from the convex patterns, obtained at Step (2), and the pattern boundaries were thus sharp and step-like. Fig. 3(c) depicts the concave pattern has the same effect on the wavy structures as the convex pattern.

3.2. Effect of substrate hardness

In order to understand the effect of the substrate rigidity on the surface wavy structures, the weight ratio of PDMS to curing agent was changed from 10:1 to 5:1. With the increase of curing agent, the solidification time for PDMS was obviously decreased and the hardness was increased at the same time. It was interesting to find the wavy structures on the hardness-improved, flat substrate were not random. As shown in Fig. 4(a), each wavy structure was placed side by side and arranged more close to parallel surface structures. The hardness-improved substrate with a single lens-like bumped pattern was also presented in Fig. 4(a). With the existence of the bumped pattern, the surface structures in Fig. 4(b), unlike those in Fig. 3(b) that showed a clear tendency of stretching radically out from the pattern boundary, tended to arrange themselves in parallel. Therefore, the effect of the substrate rigidity on the orientation of wave structures was noticeable. But how this factor affects the final orientation of the wavy structures is not clear. To understand this, a more detailed and systematic study would be required.

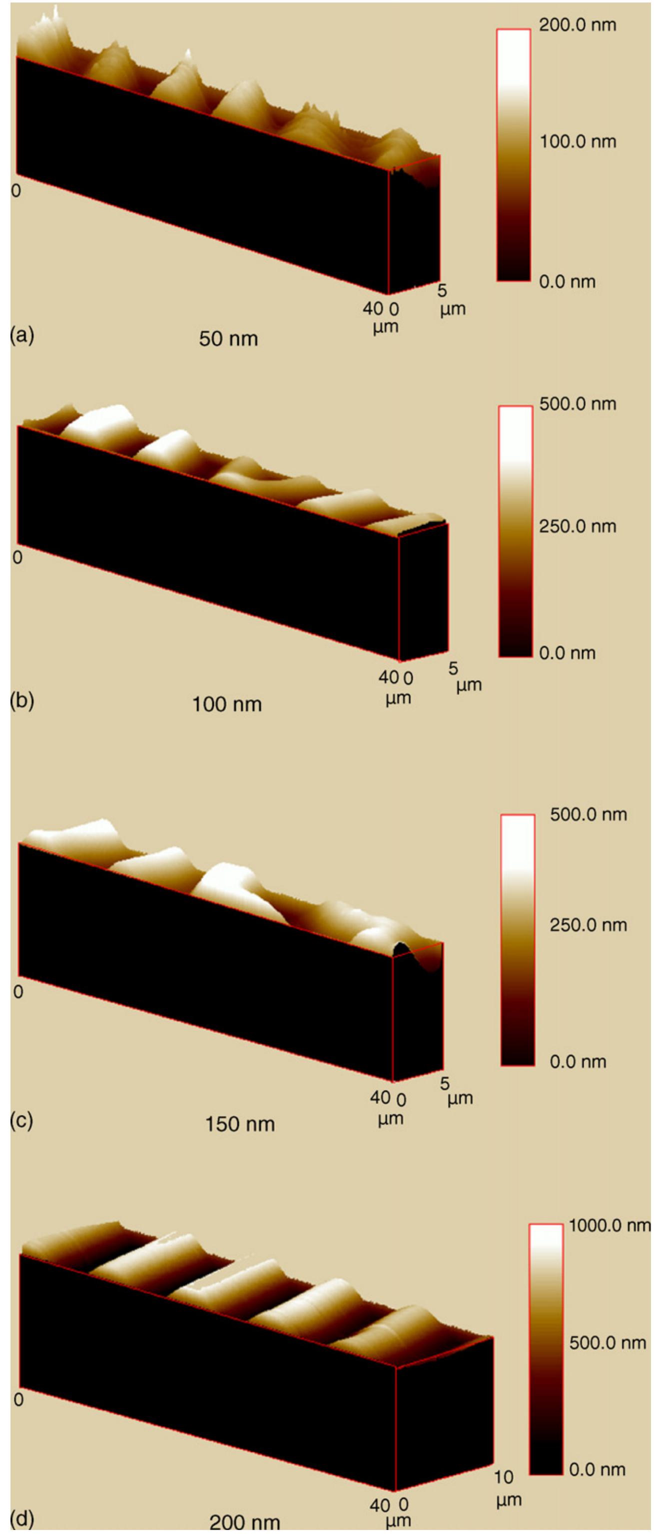

Fig. 6. AFM images showing heights of the surface structures. (a); (b); (c); and (d) correspond to figures (a); (b); (c); and (d) in Fig. 5, respectively.

3.3. Effect of thickness of metallic film

To understand the effect of the thickness of metallic film on the surface structures, the PDMS substrates deposited with different thickness of metallic films were examined. Our experiments showed that when the thickness was below 30 nm, wavy structures were hardly to be observed. However, as the thickness was larger than 30 nm, wavy structures became gradually clearer. Hence, the thickness of the metallic film can affect the development of the wavy structures. Fig. 5(a–d) show four surface images of the PDMS substrates that, respectively, covered by a gold film with film thickness of 50, 100, 150, and 200 nm. There was a circular, step-like bumped pattern that was with the diameter of 100 μm and height of 10 μm on each substrate. The observed periodicities of the wavy structures for Fig. 5(a–d) were given by 5.38, 6.25, 7.39, and 8.33 μm, respectively. These results demonstrated the periodicity of the wavy structures increased with the increase of the film thickness. Experimental data further revealed that as the film thickness was increased by 50 nm, the periodicity of wavy structures was increased roughly by 1 μm. Hence, the periodicity of wavy structures could be adjusted, to some extent, by the film thickness. The AFM images showing the surface topographies for Fig. 5(a–d) are presented correspondingly in Fig. 6(a–d). The heights of wavy structures were within the ranges of 150–200, 450–500, 550–600, and 950–1100 nm for the Au films with thickness of 50, 100, 150, and 200 nm, respectively. In addition to those on the substrate, structures on the top surface of the bumped pattern were also examined. As the film thickness was increased from 50 to 200 nm, the surface structures went from a porous structure, Fig. 5(a), to a random wavy structure, Fig. 5(d). Thus, the wavy structures are more likely to form on a flat surface without geometrical constraints or on a surface deposited with a relatively thick metallic film.

4. Conclusion

Random wavy structures were often-observable on a soft PDMS substrate covered with a metallic thin film. In order to control the orientation and periodicity of the wavy structure, three major factors, including shape of the pattern on the substrate, the hardness of the substrate, and the thickness of the deposited metallic film, that relate to formation of a surface wavy structure were discussed in this study. Results show that a random wavy surface structure could be straightforwardly formed on a flat PDMS substrate with deposition of a thin gold film. With the existence of patterns on the substrate, orientations for the surface structures close to the patterns were, however, showed certain trends. With suitable arrangement of the location, shape and size of the patterns, the surface wavy structures can be well regulated to a certain extent. As the hardness of the PDMS substrate was enhanced, the tendency of forming random wavy structures was considerably inhibited that led to a more regular and parallel arrangement of the wavy structures. The effect of thickness of metallic film on the surface structure was reflected on the periodicity and height of the wavy structures. An increase of the thickness of the Au film by 50 nm, the periodicity of wavy structures was increased roughly by 1 μm. In this study, the periodicity of the wavy structures was within the range of 5–8 μm. With suitable arrangement of pattern configurations and adjustment of substrate hardness, a compound structure, combing longitudinal patterns and transverse wavy structures, and a parallel wavy structure were fabricated. The present study thus reveals a relatively simple way of forming a designated complicate surface structure that has potential applications in fabrication of grating structures.

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