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Scalable shape-controlled fabrication of curved microstructures using a femtosecond laser wet-etching process

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ABSTRACT

Materials with curvilinear surface microstructures are highly desirable for micro-optical and biomedical devices. However, realization of such devices efficiently remains technically challenging. This paper demonstrates a facile and flexible method to fabricate curvilinear microstructures with controllable shapes and dimensions. The method composes of femtosecond laser exposures and chemical etching process with the hydrofluoric acid solutions. By fixed-point and step-in laser irradiations followed by the chemical treatments, concave microstructures with different profiles such as spherical, conical, bell-like and parabola were fabricated on silica glasses. The convex structures were replicated on polymers by the casting replication process. In this work, we used this technique to fabricate high-quality microlens arrays and high-aspect-ratio microwells which can be used in 3D cell culture. This approach offers several advantages such as high-efficient, scalable shape-controllable and easy manipulations.

1. Introduction

The ability to generate microstructures with curvilinear surfaces on transparent materials allows for fabricating various micro-optical and biomedical devices [1–3]. For example, curved microstructures on glasses and polymers can be used as microlenses which are widely used in optical communications, display and lighting systems, imaging devices and microfabrications [4–6]. In addition, microwells with curved surfaces have potential applications in three-dimensional (3D) cell culture, single cell trapping and analysis, microbioreactor arrays and lab-on-chip systems [7–9].

Several strategies have been adopted for fabricating curved microstructures, such as lithographic thermal reflow technique, gray-tone photolithography, ink-jet process, diamond milling, PDMS processes and beam direct writing [10–14]. However, these methods still have drawbacks in fabricating high-quality curved microstructures. Lithography-based techniques require expensive equipments and complicated procedures, and are difficult to fabricate high-aspect-ratio microstructures; ink-jet and PDMS process can generate spherical-shaped microstructures, but the shapes are not controllable; diamond milling and beam direct writing methods can be used for producing microstructures with tunable shapes, but suffer from long processing times. For most current microfabrication techniques, precise fabrication of scalable and shape-tunable curved microstructures with high-aspect-ratios is still challenging.

To overcome these limitations, we have developed a simple, high-efficient maskless technique for large-area gapless MLAs using a femtosecond laser wet etch (FLWE) process in the previous works [15–17]. In the FLWE process, the ultrafast laser delivers intensity- and time-controlled, programmable arranged, individual pulses to a glass chip. The sample is then subjected to wet-etch processing. The laser pulses change the physical and chemical properties of the glass in the focal spots, and the wet-etch processing that follows carves out a unique microlens array pattern. It offers several advantages: 1) ability to create high-aspect-ratio concave curved microstructures rapidly; 2) flexibility in tuning the dimensions and profiles of the structures; 3) ease of manipulation and a few fabrication procedures. This work presents a improved femtosecond laser wet-etching process (FLWE) for fabricating high-quality microlens arrays with controllable shapes especially aspherical microstructures. And these special microlens arrays are highly desired in biomedical field for example microlens arrays with high-aspect-ratio concave microstructures can be used as microwells for cell culture and analysis.

2. Experimental

The fabrication process is schematically depicted in Fig. 1. The materials used in the experiments were polished silica glass chips with dimensions of $15 \times 15 \times 2$ mm^3. The laser source was 800 nm, 30 fs and 1 kHz Ti:sapphire oscillator-amplifier system (FEMTOPOWER Compact Pro, FEMTOLASERS). The beam was focused normally onto the surface of the silica glass via an objective lens (NA = 0.5) and created the laser-induced modifications of the materials. After the laser treatments, the samples were immersed in the water-diluted hydrofluoric (HF) acid solution with a concentration of 5% for several minutes. Because of the laser-induced modifications of the materials, the laser-treated regions were chemically etched out rapidly with little damage of the

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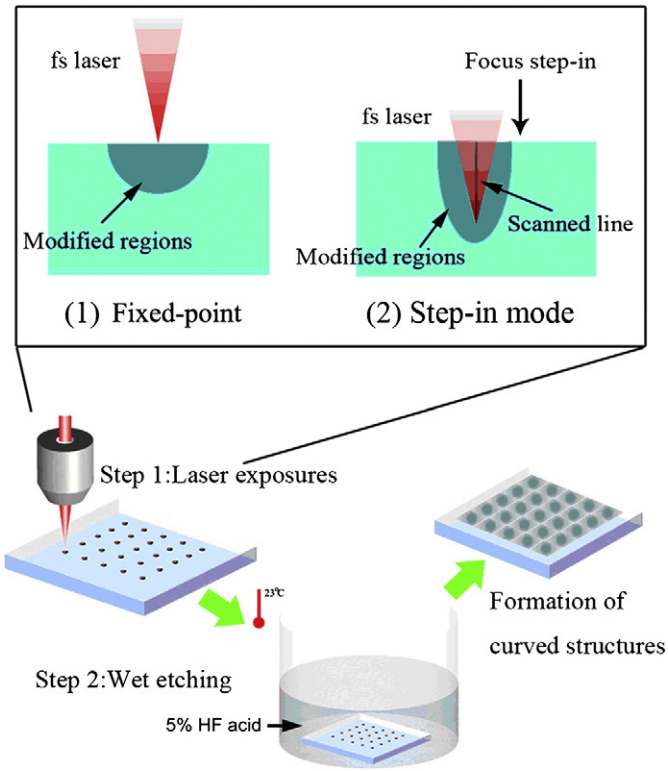

Fig. 1. Schematic diagrams of the fabrication process and the laser exposure methods.

original materials, and the concave microstructures formed. The whole etching process was monitored by an optical microscope system (OM, NIKON CV-100) equipped with a CCD camera. When the structures were completely fabricated, the samples were rinsed in the deionized water and dried by hot air.

To fabricate microlenses and high-aspect-ratio microwells, two types of laser exposure methods were used: the fixed-point irradiation and the step-in irradiation, as shown in Fig. 1. For fabricating microlenses with relatively small sag heights, fixed-point laser irradiations were adopted. The laser exposing time was controlled by the mechanical shutter. The laser power, which was tuned by a variable attenuator, ranges from 0.3 mW to 7 mW. We will demonstrate the power dependency of the lens diameter and sag height in the next section. The exposure duration was about 500 ms. In the experiments, long exposure time of each point will increase the structural uniformity of the microlenses, but decreased the fabrication efficiency. The time of 500 ms is the experimentally optimized parameter, which allows for generating 5000–6000 exposure spots per hour. So to speak, over 10,000 microlenses can be fabricated within 3 h by the above parameters.

For high-aspect-ratio microwells, step-in exposure method was used to increase the depth of the laser-induced modification. By translating the sample in the direction parallel to the optical axis (*z*-axis), the focused laser beam was drilled inside the transparent sample. Benefited from the nonlinear absorption regime of the photons, the femtosecond laser can penetrate the wide-band materials when the energy density is below the damage threshold of the materials and induce breakdown when it exceeds that value. This process, in most cases, was used to write or produce modifications and damages directly embedded inside transparent materials. Here, a line-patterned modification region was created in the sample (Fig. 1) by the focal spot of the laser pulses.

This laser-induced chemical process can produce concave microstructures on silica glasses. To fabricate convex microlenses, we used PDMS (Sylgard 184, Dow Corning) casting method: the degassed mixture of PDMS and curing agent with a ratio of 10:1 was poured on the glass molds and cured for 100 min in temperature of 90 °C. For the microwells, their PDMS replicas could be used for a second replication to create concave structures on hydrogels, which are suitable for cell culture. The results were investigated by a field-emission scanning electronic microscope (FE-SEM, JEOL JSM-7000F). The samples for SEM observations are pretreated by coating a thin film of Pt atoms with

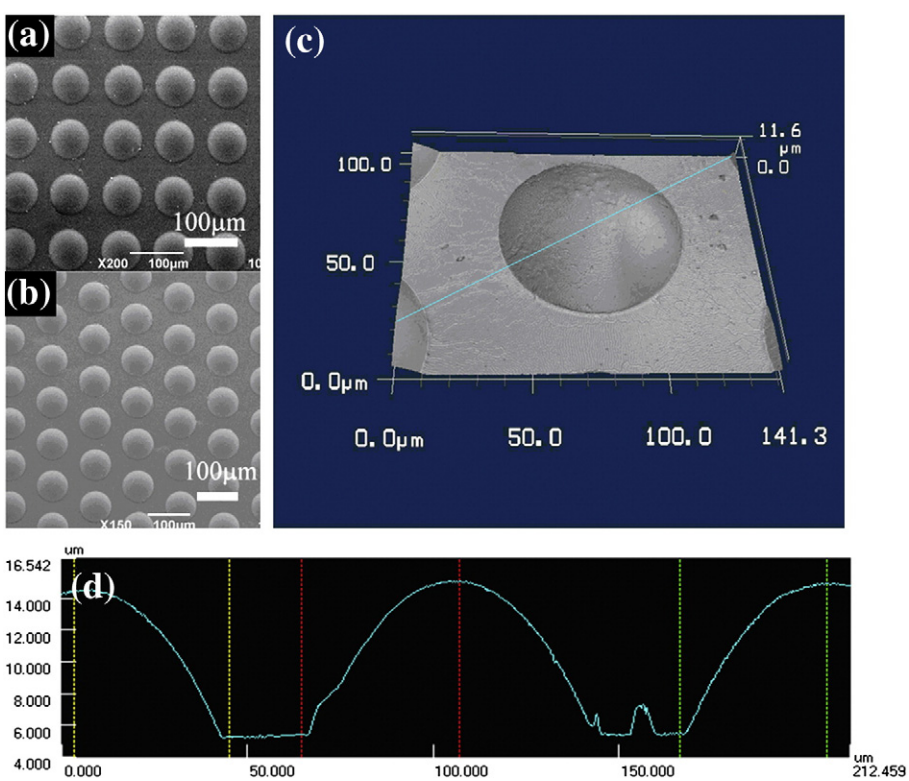

Fig. 2. Images of the fabricated microlens arrays. (a) Rectangular-packed microlens array. (b) Hexagonal-packed microlens array. (c) 3D profile of a microlens. (d) Cross-sectional profiles of the microlenses in the rectangular-packed array.

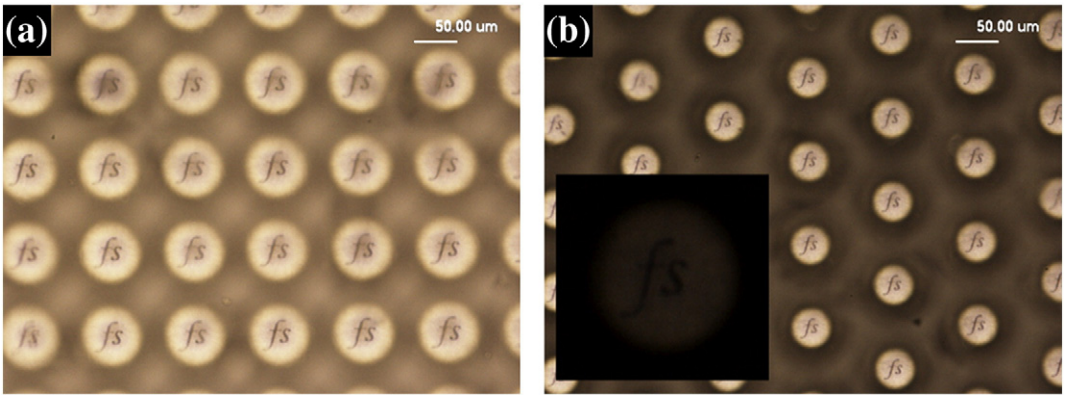

Fig. 3. Imaging properties of the microlens arrays. (a) Rectangular-packed microlens array. The images were captured by a 20× objective lens. (b) Hexagonal-packed microlens array. The inset image shows a magnification.

thickness of a few nanometers and used voltage was 20 keV. The cross-sectional and 3D profiles of the microlenses are measured by a laser scanning confocal microscope (LSCM, LASETEC S130). The imaging ability of the MLAs is obtained by the optical microscope system (OM, NIKON CV-100) with tungsten light source.

3. Results and discussion

3.1. Microlens arrays

Fig. 2 shows the results of the replicated microlens arrays fabricated by the fixed-point laser exposure method. To demonstrate the flexibility of our approach, microlens arrays with different packing manners were fabricated on PDMS, shown in Fig. 2(a) and (b). For this maskless method, the arrangement of the lenses can be easily tuned by changing the exposure positions of the laser pulses, and any pre- and post-procedures are not required. The laser power for both rectangular and hexagonal-packed arrays was 2.5 mW, and the chemical etching time spent was about 60 min. We fabricated these two microlens arrays of 2500 lenses in 2 h. We measured the dimensions of the microlenses by the laser confocal microscope, and the 3D profile and cross-sectional profiles, shown in Fig. 2(c) and (d). Because the experimental parameters for both arrays were the same, the dimensions of the microlenses are identical. The diameter and height of the microlenses are 62.5 μm and 6.2 μm, respectively. So for fixed-point laser irradiation method, the fabricating microlenses are with relatively small sag heights. We also find that the microlens arrays fabricated by fixed-point laser exposure method are with the spherical microstructures as shown in Fig. 2(d).

Compared with the laser direct writing process for microlens fabrication, except for one advantage of high efficiency, our approach provides another advantage of smooth surfaces of the microlenses. It is important for the high quality of the imaging performances of the micro-optical devices. We tested the imaging properties of the fabricated microlens arrays via an optical microscope system. The letters, *fs*, were printed on a piece of paper and inserted between the microlens arrays and the collimated tungsten light source. A CCD camera was used to capture the real images of the letters on the other side of the microlens arrays, and obtained results are shown in Fig. 3. For both rectangular and hexagonal-packed microlens arrays, the images of the letters are uniform and clear, indicating the uniformity and the smooth surfaces of the microlenses.

To demonstrate the ability of tuning the size of the microlenses, the relationship between the laser power and the size of the microlenses was investigated by an experiment. A series of the laser exposure spots were created on the sample surfaces, followed by a 30-minute HF (5%) etching. The diameters and sag heights of the formed concave structures were measured by the laser confocal microscope, and the results are plotted in Fig. 4(a) and (b), respectively. The type of fitting curve used in Fig. 4(a) and (b) is the 'B-Spline' connection of the software *Origin*. The laser power ranges from 0.5 mW to 5 mW, and the laser exposure times are 100 ms, 500 ms and 1500 ms. The diameters and sag heights of the concave microstructures increased with increasing of the laser power. Therefore, we can control the dimensions of the microlenses by using different laser powers.

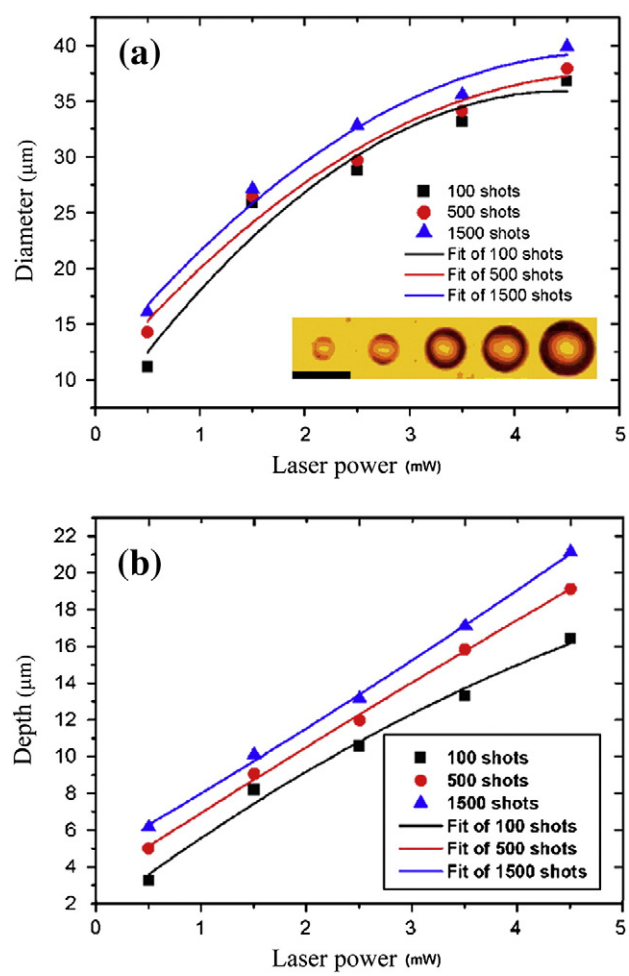

Fig. 4. Power dependencies of the diameter (a) and sag height (b) of the microlenses. The inset images in (a) show the optical microscope observations of the concave microstructures, and the scale bar equals 50 μm. The black blocks, red dots and blue triangles denote for different laser exposure times, or pulse numbers, which are 100, 500 and 1500, respectively.

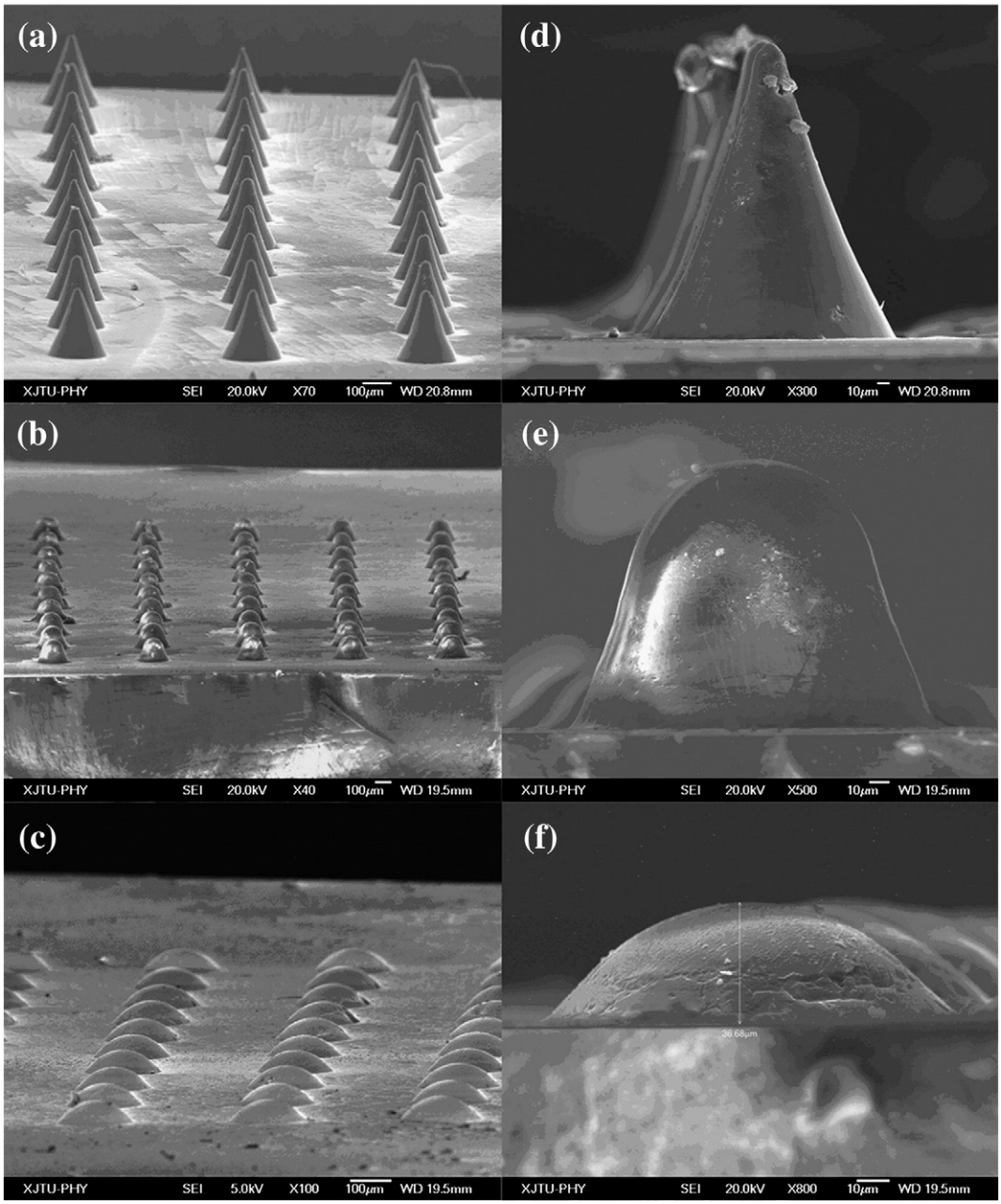

Fig. 5. PDMS replicas of the microwells. Panels (a)–(c) show the microwell arrays with different shapes. Panels (d)–(f) are magnified observations of the conical, bell-like and parabola-shaped microstructures, respectively.

3.2. High-aspect-ratio microwell arrays

As aforementioned, the high-aspect-ratio concave microstructures were generated by the step-in laser exposure method. Because the laser focal spot was used to create a line-patterned modified regions, chemical etching in the *z*-axis direction was enhanced significantly, leading to the anisotropic etching process. First of all, the materials were etched along the laser exposed lines to form narrow channels in the silica glasses. On the surface of the sample, the entrances of the channels suffer longer etching times than recesses of the channels, and consequently, the etchings in the transverse directions produced wider entrances, forming the conical-shaped microwells with sharp tips. Their PDMS reverse replicas are shown in Fig. 5(a) and (d). We used 4 mW laser pulses and the drilling depth was about 150 μm. After a 90 minute chemical treatment, the micro-cones were fabricated. The diameter and height of the structures are about 100 μm and 150 μm, respectively, and the aspect ratio reaches to 1.5:1. The aspect ratio value can be controlled by the laser-drilled depths and the etching speed in the *z*-direction, which has been proved to be related to the laser power, scanning speed and the laser polarizations [18].

When chemical etching reached to the laser irradiation endpoint in the *z*-axis direction, the vertical etching speed would reduce to the etching speed of the original glass and the increase of the depth of structures would be inconspicuous. The tips and entrances of conical-shaped structures continued to expand with the etching process and eventually formed a parabola-shaped or spherical structure. During the etching process, the cross-sectional morphologies were experienced by conical (Fig. 5(a) and (d)), bell-like (Fig. 5(b) and (e)) and parabola-shaped (Fig. 5(c) and (f)) microstructures, respectively. The aspect ratios of these structures are much larger compared to the microstructures fabricated by the fixed-point laser exposure method and our previous

reported works [15–17]. These aspherical microstructures are difficult to be created by other methods such as photolithography and ink-jet process. Actually, by smart arranging the laser-drilled depth and chemical etching times, the cross-sectional profiles of the high-aspect-ratio microwells can be tuned. Other research groups have demonstrated the advantages of the cell culture inside the microwells with spherical and conical profiles compared to the flat microstructures [9,19]. We provide here a shape-tunable fabrication process for creating 3D microwells with different curved profiles, which should be of general interest to cell aggregates, grows and differentiations.

4. Conclusions

In summary, we proposed a femtosecond-laser-induced chemical etching process to fabricate various curved microstructures. By exposing the focused laser pulses on the silica glasses with the fixed-point and step-in methods, modifications of the materials were induced by the laser-matter non-linear interactions. These modifications will significantly enhance the chemical etching speed of the hydrofluoric acid, resulting in the formation of curved concave microstructures. We demonstrated the abilities of our approach to control the size and shape of the microstructures. In the work, this method was used to fabricate high-quality microlens arrays with tunable profiles. And the high-aspect-ratio microwells fabricated in the manuscript can be used for cell aggregates, grows and differentiations. So our technique will have great potential applications in a wide range of scientific fields such as micro-optics, biomedicine and lab-on-chip systems.

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