Femtosecond laser shockwave peening ablation in liquids for hierarchical micro/nanostructuring of brittle silicon and its biological application

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Abstract
This paper presents a new technique, termed femtosecond laser shock peening ablation in liquids (fs-LSPAL), which can realize simultaneous crack micro/nanomanufacturing and hierarchical micro/nanolaser ablation, giving rise to the formation of diverse multiscale hierarchical structures, such as macroporous ratcheted structures and en échelon microfringes decorated with parabolic nanoripples. Through analysis of surface morphologies, many phenomena have been confirmed to take place during fs-LSPAL, including en échelon cracks, nanostriation, ripple densification, crack branching, and selective formation of high spatial frequency laser-induced periodic surface structures of 100–200 nm in period. At a high laser power of 700 mW, fs-LSPAL at scanning speeds of 0.2 mm s−1 and 1 mm s−1 enables the generation of height-fluctuated and height-homogeneous hierarchical structures, respectively. The height-fluctuated structures can be used to induce ‘colony’ aggregates of embryonic EB3 stem cells. At 200 mW, fs-LSPAL at 1 mm s−1 is capable of producing homogeneous tilt macroporous structures with cracked structures interleaved among them, which are the synergistic effects of bubble-induced light refraction/reflection ablation and cracks. As shown in this paper, the conventional laser ablation technique integrated with its self-driven unconventional cracking under extreme conditions expands the horizons of extreme manufacturing and offers more opportunities for complex surface structuring, which can potentially be used for biological applications.

Keywords: femtosecond laser shock peening ablation, shockwaves, macroporous, en échelon crack, striations, brittle materials, stem cell culture

(Some figures may appear in colour only in the online journal)
1. Introduction

Micro/nanofabrication techniques are the foundation of many technology-based applications in both academia and industry [1], and the demand for innovation in micro/nanofabrication technologies is ongoing. Conventional micro/nanofabrication techniques can be classified as ‘lithographic’ (i.e. soft lithography [2], etching [3], and nanoimprint lithography [4], focused ion beam lithography [5], and electron beam lithography [6]) and ‘nonlithographic’ (including laser ablation/processing [7, 8], cracking/fracture [9], wrinkling/buckling [10], folding [11], and electrospinning [12]). Much effort has been devoted to the integration of two techniques [13–15] for saving time and costs associated with the micro/nanofabrication of irregular, complex, or hierarchical structures that fill the gaps in the capability of conventional techniques.

Of all the resources (i.e. focused ion beam, electron beam, and laser beam) available for the innovation and upgrading of techniques, laser ablation/processing is the most attractive because of the large number of low-cost regulators that can be imported, in situ generation of multiple stimuli, and simultaneous material modification. Versatile processing can be performed based on laser/processing parameters [16], beam profiles (i.e. Gaussian beam, vortex beam, planar beam, Bessel beam [17], and pulse trains), and tunable environments (i.e. air, gases, vacuum, or countless liquids with and without an electrical or magnetic field [16]). In particular, during ablation by the interaction of matter with an intense laser beam, an extremely high-pressure, high-temperature (HPHT) environment can be generated, resulting in unique thermal/interfacemechanical dynamics (i.e. dewetting [14], capillary force [18, 19], shockwave peening [20], and Marangoni bursting [21]). Hence, laser ablation is a promising technique for creating unique hierarchical micro/nanostructures in which laser direct structuring and simultaneous generation of stimuli may collaboratively play crucial roles.

Simplicity is significantly important in terms of cost-effectiveness. In this regard, one of the ideal factors is the stimuli generated during laser-matter interactions in liquids, such as bubbles and shockwaves. Cracks can be induced by pressure from shockwaves generated during laser ablation. Shockwaves spontaneously form after the plasma phase. The pressure of shockwaves can reach GPa in amplitude [16]. While performing laser ablation in liquids (LAL), the collapse of cavitation bubbles offers an additional source of shockwaves [22], whose amplitudes can exceed 107 Pa [23]. A shockwave-based technique called laser shock peening (LSP), which can be traced back to the 1960s [20, 24], has been used to treat various metals to improve their mechanical properties, such as fatigue performance and hardness [25]. In contrast to metals, LSP treatment of brittle materials, such as silicon (Si), has seldom been studied. Cheng et al investigated the plastic deformation of Si induced by heat-assisted LSP using a nanosecond (ns) laser [26]. They found that LSP performed at temperatures below 750 K completely broke Si into powder pieces, while LSP at 850 K induced strong dislocations in Si crystals with 20–500 nm spacings [26]. This work indicated that LSP can yield surface cracking, but the undesirable mechanical damage to the workpiece must be inhibited. A compressive residual stress layer as thick as ~1 mm is produced during ns-LSP. While it is only microscale for femtosecond (fs) LSP [27], it is more advantageous in generating high-pressure shockwaves, two orders higher than that generated by ns-LSP [28]. Although there have been no reports so far, fs laser shock peening ablation in liquids (fs-LSPAL), which enables crack-induced nanostructuring of brittle materials during laser ablation, is highly probable and interesting. If a new technique is developed, questions spontaneously arise regarding its structuring capacities, mechanism, potential applications, and differences as compared to related techniques, such as fs-LSP.

It is well known that cellular morphologies strongly depend on surface topography. For example, Simitzi et al found that laser structuring can significantly promote the proliferation and differentiation of PC12 cells on Si as compared to flat surfaces, irrespective of geometrical characteristics [29]. Yiannakou et al found that Si high spatial frequency laser-induced periodic surface structures (HSFLs) formed by fs-LAL are cell-repellent while hierarchical micro/nanostructures consisting of microprotrusions and HSFLs are cell-philic for Schwann cells [30]. Hence, novel surface structures produced by fs-LSPAL are expected to be capable of controlling cellular behaviors.

This work explores the possibility of using fs-LSPAL for the creation of unique hierarchical micro/nanostructures with macropores among them, provides insights into the events occurring during fs-LSPAL, and seeks answers to the following questions.

(1) What morphologies are typically induced by cracks, and how are different crack structures obtained?

(2) How do the grooves break; and what roles do shockwaves play in the cracking, including the breaking mechanism and the propagation paths of shockwaves in microgrooves? Groove breaking is normally accompanied by the generation of micropowders, which are good precursors for laser melting in liquids [31] to generate submicron spheres. The dislocated powders are good ‘trackers’ for gaining insight into understanding how grooves break during fs laser ablation in liquids (fs-LAL).

(3) During fs-LAL, HSFLs are easy to induce on microstructures [32]. Is it questionable whether HSFLs can still be induced on fractured structures and whether the decoration of HSFLs is structure dependent?

(4) What are the potential applications of fs-LSPAL for the resulting structures?

To explore the answers to these questions, fs-LSPAL of Si was used in this work. In sections 3.1 and 3.2, scanning electron microscopy (SEM) morphologies of surface hierarchical micro/nanostructures obtained by fs-LSPAL at a fixed laser power of 700 mW and scan speeds of 0.2 mm s−1, 0.5 mm s−1, and 1 mm s−1 are analyzed in detail. In section 3.3, key factors and mechanisms of en échelon cracking, restructuring of HSFLs, and pearl-necklace-like structures are discussed. In section 4, the potential applications of fs-LSPAL creating...
novel homogeneously macroporous structures and manipulating the cellular behaviors of embryonic (EB3) stem cells are presented. In section 5, the differences between fs-LSP and fs-LSPAL are briefly discussed.

2. Experimental setup

2.1. Laser experiments

A fs laser system (fiber-chirped pulse amplification (FCPA), μJewel D-1000-UG3, IMRA America Inc. Ann Arbor, MI, USA) with a pulse duration, wavelength, and repetition rate of 457 fs, 1045 nm, and 100 kHz, respectively, was used for fs-LAL. A 20x objective lens (numerical aperture: 0.4, Mitutoyo, Kawasaki, Japan) was used to focus the laser beam on a single-crystalline Si substrate that was placed inside a culture dish (Φ = 45 mm; 20 mm height) filled with 8 ml of water. The liquid thickness (liquid layer above the target surface) was kept at 5 mm above the target surface. The laser powers were set at 700 mW and 200 mW with a pulse energy of 7 μJ and 2 μJ. The laser spot size was estimated to be 3.4 μm based on λ = 1045 nm and M² = 1.1 (specification provided by the laser manufacturer) of our laser system and NA = 0.42 of the objective lens used. The fluences were then calculated to be 77.14 J cm⁻² and 22.04 J cm⁻². An area of 2 mm × 2 mm was scanned using the line-by-line method for detailed study of surface morphologies. The scanning line intervals (also termed as hatch offset [33]) were 5 μm and 15 μm for fs-LSPAL at 700 mW and 5 μm for fs-LSPAL at 200 mW. The scanning speeds were 0.2 mm s⁻¹, 0.5 mm s⁻¹, and 1 mm s⁻¹. To study the cellular behaviors on different cracked structures, two samples (1 mm × 1 mm) were prepared by fs-LSPAL at 700 mW with a fixed scanning speed of 0.2 mm s⁻¹ and scanning intervals of 5 μm and 15 μm. SEM (Thermo Scientific™, Quattro ESEM™, Tokyo, Japan) equipped with a navigation camera (Nav-Cam) detector and infrared (IR) camera for sample navigation and review in chamber and Raman spectroscopy (LabRAM, Horiba, helium-neon (He-Ne) laser, 632 nm, Tokyo, Japan) were used to characterize the micro/nanostructures of the ablated substrates.

2.2. Biological experiments

EB3 stem cells were used to test the cellular behaviors on two samples. The surface structures were coated with gelatin. The 10⁶ EB3 stem cells were cultured on the structures and then fixed by 4% paraformaldehyde for 15 min. For the cells’ morphological characterization, the fixed samples were permeabilized by 0.1% Triton™ X-100, washed with phosphate buffered saline (PBS), and actin filaments (F-actin) were stained with phalloidin (Invitrogen™) for 30 min at room temperature (dilution: 1:1000). Then, the samples were washed by PBS and stained with Hoechst 33342 (dilution: 1:5000). After characterization of the cellular morphologies by a fluorescence microscope (Olympus IX71), the samples were dehydrated using increasing concentrations of ethanol to replace PBS and finally using 100% ethanol. After replacing the ethanol using hexamethyldisilazane (HMDS), the samples were dried in a fume hood for SEM characterization.

3. Hierarchical micro/nanostructures and formation mechanisms

3.1. Hierarchical micro/nanostructures

3.1.1. Macroporous cracked structures. Figure 1 shows the structures obtained by fs-LSPAL of Si in water at a laser power of 700 mW and scan speeds of 0.2 mm s⁻¹, 0.5 mm s⁻¹, and 1 mm s⁻¹ with a scanning interval of 15 μm. Most grooves are broken, while only a few grooves are intact or partially broken (green arrows in figures 1(a)–(c)), whose edges appear white due to the formation of HSFLs [32]. Macropores located between two adjacent broken grooves are more clearly seen at higher magnifications (figures 1(d)–(f)). The gradually reduced pore size with increased scan speeds indicates that the pore size can be modulated by changing the scanning speed at a fixed scanning line interval and laser power. Besides sporadic spherical macropores, bent (pink arrows in figure 1(d)), elongated (yellow arrows in figure 1(e)), rectangular (green arrows in figure 1(e)), square (a blue arrow in figure 1(e)), and zig-zag-like (white arrows in figures 1(e) and (f)) macropores are also produced. These macropores are not as uniform as those produced on Si [34–36] and aluminum (Al) [37] surfaces by laser ablation in air, indicating that it is highly possible to cause the deviation in direction of the incident laser pulses by the cavitation bubbles generated during LAL [38].

Figures 1(g)–(i) show the side views of surface morphologies obtained by fs-LSPAL at a laser power of 700 mW and scan speeds of 0.2 mm s⁻¹, 0.5 mm s⁻¹, and 1 mm s⁻¹, observed by tilting the sample at 30° in the Y-Z plane (laser scanning is along the X-axis). The grooves are ratcheted with drastic fluctuations in microstructure height, irrespective of scan speeds. The ratcheted grooves are composed of hierarchical curved microstructures propagating slantly from the top to the bottom of the grooves (regions pointed to by the pink arrows (figures 1(j)–(l)), as observed with a 30° tilt in the X-Z plane). The lengths of the hierarchical microstructures depend on the scan speed. Faster scanning allows the formation of longer curved microstructures (figures 1(j)–(l)). At the higher speeds of 0.5 mm s⁻¹ and 1 mm s⁻¹, curved microstructures are consecutive on the same groove (figures 1(k) and (l)), while curved microstructures are isolated when the scan speed is 0.2 mm s⁻¹ (figure 1(j)). The formation of such microstructures is caused by cracking induced during fs-LSPAL since they are very similar to the curved crack structures on Si induced by pressure [39] or bend [40] loading. However, pressure and bend loadings are only capable of generating two-dimensional (2D) curved microstructures [40]. This work reports, for the first time, the feasibility of inducing 3D crack structuring on slanted side walls of ratcheted microstructures by fs-LSPAL.

Figure 2(a) shows a typical structure (length/width of 40/12 μm) consisting of parabolic or quarter-ellipse-shaped structures (ripple marks [41]) at both the microscale and nanoscale induced by an échelon fringe cracking during fs-LSPAL.
Figure 1. (a)–(l) SEM images showing the surface morphologies obtained by fs-LSPAL of Si in water at 700 mW with a scanning interval of 15 μm at scan speeds of 0.2 mm s⁻¹, 0.5 mm s⁻¹, and 1 mm s⁻¹, respectively. (a)–(c), (d)–(f) Images observed from the top; (g)–(i), (j)–(l) were taken with the samples at a 30° tilt in different directions.

Fitting lines to the quarter-ellipse-shaped structures are shown in figure 2(b). Three kinds of quarter-ellipse-shaped structures can be identified, as marked by red, pink, and green. The red lines (figure 2(b)) start from the left corner of the groove and propagate from left to right to form the primary skeleton of the crack regions in the X-Y plane. A series of renewed cracks along parts of existing crack front lines originates from the same starting point [41]. Such fitting lines are called Wallner lines [40, 42] from the fractographic perspective, which are the undulations of the crack front aroused by the interaction between a propagating crack front and the shear waves emanating from surface imperfections and irregularities [43]. Wallner lines are the indicators of the traces of crack fronts. The shape of Wallner lines strongly depends on crack velocities [40]. The similarity of the red Wallner lines shown in figure 2(b) to those shown in Zhao et al. [40], indicates that the velocities of the crack fronts are in the range of 1000–3000 m s⁻¹.

The green lines and the regions between them, marked by the double-sided green arrows, are two families of delicate ripple parabolic/elliptical furrows and ridge nanostructures (figures 2(c)–(f)). Fourteen parabolic/elliptical ridges with intervals of 189 nm, 170 nm, 398 nm, 170 nm, 294 nm, 69 nm, 75 nm, 111 nm, 67 nm, 67 nm, 67 nm, 99 nm, 93 nm, and 85 nm (average value of 140 ± 95 nm), can be identified in figure 2(d). In the places where microcracking terminates (region pointed to by a green arrow in figure 2(e)), a high density (24 ripples with a whole width of 1.4 μm and average ripple width of 58 nm) of nanostructures is also generated, being the ripple marks on the exfoliation joints [41]. Their intervals change from 107 nm to 24 nm as the nanocracking propagates from the left to the right (figure 2(f)). The propagation of the principal microcracks is often accompanied by the imprint of nanostructures caused by nanocracks (figures 2(c) and (e)) induced by localized pulse-like nanoscale waves [44]. It is believed that the tips of cracks induce an increase in the material temperature [45], well above the glass transition temperature (T_g), thus allowing the printing of ripple nanostructures. Such nanoscale wobbling of the crack tip has also been observed on a brittle bulk metallic glass [45]. Figure 2(e) displays the formation of stepped-fringe microstructures on the sidewalls (the region pointed to by the pink arrow), which are en échelon fringes [41]. The joint lines (pink lines) of such stepped fringe structures expand upward, indicating the increased amplitude of shear stresses as fs-LSPAL proceeds.
En Échelon Fringe Crack
Renewed Fracture Propagation and Ripple Marks on Exfoliation Joints

(a) Starting point
(b) Propagation
(c) Top view
(d) Side view with a scan interval of 15 µm
(e) Wallner lines drawn from the ripple marks in (a)
(f) Further enlarged images showing the ripple nanostructures

En Échelon Fringes with Parabolic/Elliptical Ripple Marks

(g) Top view
(h) 30° tilt
(i) 30° tilt

En Échelon Fringes with Bent Ripple Marks

(j) Top view
(k) 30° tilt
(l) 30° tilt

En Échelon Fringes with Striation Arrest Marks

(m) Top view
(n) 30° tilt
(o) 30° tilt

Figure 2. En échelon cracks induced by fs-LSPAL at a fixed laser power of 700 mW and scan speeds of 0.2 (a)–(i) and 1 mm s\(^{-1}\) (j)–(o) with a scan interval of 15 µm (a)–(f). Renewed fracture propagation and ripple marks on en échelon fringes. (a) Left-to-right propagated crack induced a series of parabolic/elliptical furrows and ridges (ripple marks). (b) Wallner lines of the surface structures drawn from the ripple marks in (a). (c), (e) Enlargement of the regions pointed to by the pink and green arrows in (a), respectively. (d), (f) Further enlarged images showing the ripple nanostructures in (c) and (e). (g)–(i), (j)–(l), (m)–(o) Side view of en échelon stepped fringes with parabolic/elliptical ripple marks, bent ripple marks, and striation-arrest marks, respectively. Images were taken from the side with the samples at a 30° tilt.

Three typical kinds of en échelon stepped fringes can be seen from the side view, as shown in figures 2(g)–(o). Figure 2(g) shows microstructures consisting of six-step fringe (numbered in figures 2(g) and (h)) produced by a crack propagating from right to left. The side view of such structures clearly shows that the crack first goes from the upper right slantly to the central bottom in the groove and then propagates to the upper left. Figure 2(h) shows that the starting points of subsequent cracks initiate from the middle part of the previous en échelon crack fringe. Note that the heights of the fringes gradually become smaller, which means that the amplitude of the crack for the 3rd–6th fringes gradually becomes smaller after it reaches the deepest region (second fringe) and then changes its propagation direction. Nanoripple marks are found on both the downstream and upstream regions of the stepped microfringe (figure 2(i)), corresponding to the region pointed...
Figure 3. SEM images showing rotated (a)–(c), zigzag (d)–(f), staircase-like (g)–(i), and spiral striation-arrest marks (j)–(l) obtained by fs-LSPAL at 700 mW and 0.2 mm s$^{-1}$ with a 15 µm scanning interval. Side view with samples at a 30$^\circ$ tilt.

...to by a green arrow in figure 2(h). The periods of nanoripples on the downstream part are in the range of 100–200 nm (pointed to by the pink arrow in 2(i)), much larger than the ripples of 50 nm in period on the upstream side (pointed to by the green arrow), which indicates a decrease in amplitude of the nanocrack after the formation of a stepped fringe. Figures 2(j) and (k) show another kind of en échelon crack structure obtained by fs-LSPAL at 700 mW and 1 mm s$^{-1}$, which is characterized by only two fringes. One fringe is composed of 95$^\circ$ strong bent ripples fringes (figure 2(l)).

Figure 2(m) shows the third kind of en échelon five-stepped fringes with a height of 9.6 µm produced by fs-LSPAL at 700 mW and 1 mm s$^{-1}$ where no gradual height-changed fringes are found. Instead, an échelon stepped fringes feature sharp stair-like microstructures (figure 2(n)), indicating a discontinuous abrupt propagation of cracks while they propagate upward [46]. The sidewalls of the abrupt fringes are characterized by oblique striation-arrest nanomarks, which are oriented perpendicular to the pink arrow in figure 2(o). In addition, seven striation-arrest nanomarks (striation heights of 63 nm, 50 nm, 18 nm, 13 nm, 22 nm, 27 nm, and 9 nm), whose orientations are perpendicular to the blue arrow in figure 2(o), are located on the top part of the stepped fringe. Hence, a simultaneous propagation of the crack along both of the directions indicated by the pink and blue arrows is confirmed.

Striation-arrest marks are also capable of being rotated, zigzag, staircase-like, and spiral, as shown in figure 3. Figures 3(a) and (b) show the top and side views of striation marks rotated anticlockwise (area: 10 × 18 µm$^2$) in the region, as pointed to by the pink arrow in figure 1(l). The higher magnification image in figure 3(c) indicates the gradually decreased heights (from 216 nm to 5 nm) of these striation nanostructures. When an additional crack takes place near the boundary of a large-scale en échelon crack (figure 3(d)), zigzag striation-arrest marks are generated (figure 3(e)). The height of the striations decreases from 54 nm to 5 nm (figure 3(f)). Figures 3(g) and (h) indicate that the striation phenomenon can take place on a trapezoidal microstructure which forms by a sliding crack. The boundary of staircase-like nanostructures also yields many substriations of tens of nm in length (pointed to by the blue arrows in figure 3(i)). Such nanostructures are twist hackles, corresponding to the leading portion of a crack experiencing the highest tensile stress [47]. Figure 3(j) presents the possibility of inducing multidirectional en échelon fringes and spiral striation structures above them. The 1st–3rd fringe layers share the same starting point and propagation direction, while the 4th and the 5th layered fringes are orientated very differently. On
the turning joint areas of the fringe-layered strands, pangolin-like patch striations are generated (figures 3(k) and (l)), which offer evidence for the occurrence of strongly tilted rotating cracks with small twist angles.

In addition to spiral striations (figure 3(a)), staircase-like spiral ripple arrays are also generated on the clockwise spiral en échelon fringes (figures 4(a)–(f)). The heights of en échelon fringes gradually increase from the bottom to the top (412 nm, 458 nm, 682 nm, and 1027 nm for the 1st–4th fringes), together with an increase in the height of the ripple nanostructures. Figure 4(b) shows the enlarged morphologies of the nanoripples on the 1st and 2nd fringes. There are two directional ripples on the 1st fringe, as indicated by the pink and green lines in figure 4(b). Eight ripples of the 1st fringe (pink rectangle in figure 4(b)) are enlarged and shown in figure 4(c). The ripple intervals are 18.7 nm, 19.5 nm, 19.5 nm, 21.1 nm, 30.3 nm, 17.0 nm, 23.7 nm, and 28.6 nm with an average value of $22.3 \pm 4.8$ nm. Figure 4(d) shows the straight ripple-arrest marks on the joint position of the 1st and 2nd fringes, where twice denser ripples are found on the left part because of the termination of one left-to-right propagating ripple in the region pointed to by the green arrow. Figure 4(e) displays the curved ripples on the 3rd fringe where two directional ripples come across at the bottom (marked by the pink and green lines). The crack along the green line is too weak to distinguish the resultant ripples. The interval of the main nanoripples parallel to the pink line increases from 16 (near the pink line) to 192 nm (3rd and 4th fringes) and decreases to 88 nm (1st and 2nd fringes) as the height increases. On the 4th fringe, the height of main fringe increases to ~250 nm maximum. The variation in the heights of ripples may be attributed to the change in crack velocity [47]. In line with the phenomenon shown in figure 4(i), nanostriations with intervals of 25–40 nm are produced at the edge of the main fringe due to the high tensile stress there.

Figure 4(d) gives an inspiration for densifying ripples by the cross-connection approach. Figures 4(h) and (i) present a representative of a triple densification of ripples occurring on a sharp fringe of 1.2 μm in height (figure 4(h)). Within the region marked by the dashed lines in figure 4(i), the density of ripples on the left is triple of that on the right because two additional ripples are located and terminated at the position marked by the green arrow. Hence, the interval of ripples is around 18 nm, one-third of the 54 nm of ripples on the right. Twice the density of ripple marks are also found with the terminated ripples marked by the pink arrows. Based on the analysis of figure 4, it is speculated that: (1) if two or more nanoripple-involved cracks with the same crack amplitude and speed can be triggered in the same region, a ripple network can be produced; and (2) if it is possible to induce multiple ripple-arrest marks from both the left and right parts of a microcrack and then to overlap them, very fine nanoarray arrays with resolutions of several nm can be generated in a short time, more efficiently than conventional lithographies.

Crack branching [47], which often occurs when two crack fronts with different propagation directions encounter each
3.2. Crack path, dislocated powders, and selective HSFL formation on cracked structures

3.2.1. Crack paths and dislocated powders. In the last section, we only showed the morphologies of hierarchical micro/nanostructures induced by en échelon fringe cracking and sliding cracking. Little is known about how cracks initiate and how micropowders are dislocated from the grooves. To this end, partially broken grooves are characterized to identify the crack paths during fs-LSPAL. Figures 6(a)–(d) display three partially broken grooves generated by fs-LSPAL at scan speeds of 0.2 mm s\(^{-1}\), 0.5 mm s\(^{-1}\), and 1 mm s\(^{-1}\) with a fixed laser power of 700 mW. Their top surfaces are corrugated (figures 6(a) and (g)) or oblique (figure 6(d)) because of the dislocation of powders induced by cracks. Meanwhile, small irregular holes (resulting from powder dislocation) with widths of hundreds of nm and lengths around 1 µm (figure 6(c)) are found on the sidewall of the partially broken groove (figure 6(b)). They connect to each other to form a long crack path. Enlarged images of the sidewalls on other partially broken grooves indicate dislocation of different shapes of powders with sizes ranging from 2 µm to 10 µm; and they are characterized by sharp, zigzag, and sometimes curved boundaries (figures 6(e), (f), (h) and (i)). The cracks are generated along the facets of the dislocated powders. A series of powder dislocations induce cracks with lengths of tens of µm (figures 6(a), (d), and (g)).

Based on the results described above, we speculate that as long as a loop-lock crack is induced over the whole groove, the dislocation of large pieces of powder (tens of µm) is highly possible. Such speculation is verified by the discovery of many pieces of powder captured or trapped inside the broken grooves, as shown in figures 6(j) and (o)–(r), where the broken grooves act as powder ‘trappers.’ Figure 6(j) shows a curved powder 7.3 µm in width and 25.0 µm in length. This dislocated powder underwent a series of cracks and fractures in terms of Wallner lines (figure 6(k)) and striations (figure 6(l)) in the upper parts and in the center part where a smooth concave crater was produced (figure 6(m)). The orthogonal orientation of the cracks in figure 6(n) relative to that of the striations shown in figure 6(k) indicate that at least two cracks in orthogonal directions have already taken place. Many large particles of 200–300 nm and oval nanostructures 70–80 nm in length (figure 6(m)) are located above the smooth crater, which may be the result of in situ deposition of particles generated during fs-LSPAL. The particles generated by laser ablation normally undergo particle nucleation and growth [48], different from the powder generated from crack-induced mechanical peeling of surface structures. Figures 6(o) and (p) display a curved powder (length and width: 24.3 µm and 9.5 µm, respectively) trapped between two adjacent grooves and a micropowder with an apparent U-shaped crevice, which is the joint area of two consecutive cracks. The very sharp zigzag boundary of the powder in figure 6(p) indicates that its dislocation is caused by two cracks in different directions. Figure 6(q) shows that the available trap regions are not limited to the groove gap. The slanted crack crater at the bottom of a groove also participates in catching a larger piece of powder, 36 µm in length, with the aid of the adjacent broken groove. One large elongated piece of powder, as long as ~41 µm, is shown in figure 6(r), which indicates that a large piece of the groove can be pelt off by cracks. Identification of powder dislocations and their induced crack path (figures 6(a)–(i)) and the shapes and surface states of large dislocated powders (figures 6(j)–(r)) provide very valuable information to identify the crack mechanisms, which are discussed in section 3.3.

3.2.2. Selective HSFL formation on cracked structures. In our previous work, HSFLs were found to fully cover both the crests and troughs of noncracked microgrooves [32]. It is expected that groove cracks should generate structures with smooth surfaces free of HSFLs. However, HSFLs can still be found; and their formation significantly depends on the scan speed and structure orientation. HSFLs are found at a lower speed of 0.2 mm s\(^{-1}\), mainly on the sidewalls (Y-Z plane) of cliff-like or slanted planes in a closed space (figures 7(a) and (c)) and the boundaries (figures 7(b) and (d)).
Crack paths of two partially broken grooves obtained by fs-LSPAL at 0.2 mm s$^{-1}$, 0.5 mm s$^{-1}$, and 1 mm s$^{-1}$ with a 15 µm scanning interval. Powders obtained by fs-LSPAL at 0.2 mm s$^{-1}$. Enlarged images of the structure in (j). Explosion patterns in (b) indicate the places where the spallations of nanopowders occurred. Images were taken from a side view at a 30° tilt and top view, respectively.

Explosion patterns in (b) indicate the places where the spallations of nanopowders occurred. Images (e)–(p) were taken at a tilt angle of 30°. The direction of light polarization is indicated in (c).

Of cracks, rather than the crests of cracked microstructures (figures 7(a) and (d)). Nevertheless, the orientation of HSFLs changes with the height gradient of microstructures; and some HSFLs are curved (figures 7(e) and (f)). No HSFLs are found on the sidewalls of X-Z planes, which is very obvious on the cliff-like microstructures shown in figure 7(e). Figures 7(g) and (h) show that selective HSFL formation on the microstructures in the X-Z plane still occur at a higher scan speed of 0.5 mm s$^{-1}$ but are unavailable in the X-Y plane.

Figures 7(i)–(l) show that parabolic/elliptical ridges are also capable of being restructured into pearl-necklace-like particle arrays. Some parabolic/elliptical ridges are transformed into spherical particle arrays (figures 7(j) and (l)). The particle sizes are in the range of 100–185 nm, while the widths of the ridges in which they reside range from 150 nm to 300 nm, a little larger than the particle sizes. In addition, figure 2(d) shows that parabolic/elliptical ridges can also transform into HSFL ripples. This means it is
possible to manipulate the width of parabolic/elliptical ridges to restructure them into HSFLs or particle arrays. As the scan speed is increased to 0.5 mm s\(^{-1}\) (figure 7(m)) and 1 mm s\(^{-1}\) (figure 7(o)), the homogeneity of HSFLs becomes much poorer since the HSFLs become chaotically bent and the particles become elongated, although parabolic/elliptical ridges still seem to be restructured into HSFLs or particles (figures 7(n) and (p)). This phenomenon is caused by stronger perturbations of liquids during high scan speed fs-LSPAL. On the even microstructures, the orientation of HSFLs is perpendicular to the direction of light polarization. But on the cliff-like microstructures with height gradients, laser-induced periodic surface structures (LIPSS) are tilted at 20°, in accordance with our previous report [32].

In our previous report, the necessity of surface melting for HSFL formation [32] was demonstrated, so a Raman peak of amorphous Si is a good indicator of surface melting. It is speculated that the Raman spectra of HSFL-decorated and HSFL-free regions are different. Figure 8 shows the Raman spectra of the tested structures (inset optical images) obtained by fs-LSPAL at a scan speed of 0.2 mm s\(^{-1}\). In an HSFL-free region (figure 8(a)), despite a strong elongated scattering of the laser light, three Raman peaks at ~300 cm\(^{-1}\), 519.7 cm\(^{-1}\), and ~960 cm\(^{-1}\) belonging to the two transverse acoustic (2TA) mode, transverse optical phonon (TO), and two transverse optical (2TO) modes, respectively, are observed, which are the intrinsic Raman peaks of Si [49]. In an HSFL-rich region, a shallow amorphous Si peak at 480 cm\(^{-1}\) appears (figure 8(b)) in addition to intrinsic Si peaks, which come from the elongated scattered laser on the microstructures (the white region in the inset image), enabling the detection of the Raman signal of HSFLs nearby. In the region fully decorated by HSFLs (figure 8(c)), an obvious amorphous Si peak is observed. Meanwhile, the TO peak is blueshifted to 516.3 cm\(^{-1}\). A blueshift of the TO mode is attributed to either the quantum confinement from the Si quantum dots, less than 10 nm in size, a lattice expansion induced by laser-induced thermal heating [50], or the tensile stress exerted to Si crystals [51]. Also, the peak intensity of the TO mode significantly decreases compared to those (figures 8(a) and (b)) measured on smooth crack surfaces, which means that HSFLs have very high absorbance or strongly scatter laser light. An amorphous Si peak with much lower intensity is observed while testing the macropores whose sidewalls are full of HSFLs (figure 8(d)). Thus, compared to HSFLs themselves, HSFL-decorated macropores enable much stronger light trapping. Based on the Raman spectra shown in figure 8, it is proven that HSFL formation is accompanied by surface amorphization.
3.3. Key factors and mechanisms of cracking and HSFL restructuring

Both the partially broken grooves and the large dislocated powders help us to know how powders get peeled from the grooves, based on which we propose the crucial roles shockwaves play in cracking and selective HSFL restructuring during fs-LSPAL.

3.3.1. Shockwave sources

3.3.1.1. Ablation shockwaves. During LALs, strong shockwaves are always produced after the plasma phase. These ablation shockwaves propagate at a speed of 1500 m s\(^{-1}\) in water [16]. The pressure amplitude can reach up to the order of GPa [52]. Figures 9(a)–(c) provide evidence of the existence of ablation shockwaves on broken grooves. Parallel ripples with periods of hundreds of nm (figure 9(b)) and a maximum length of 7.5 \(\mu\)m are located on the fringe microstructure (figure 9(c)). A spot crater with a diameter of \(-1 \mu\)m is considered to be the source for the ablation shockwaves because it is surrounded by parallel ripples with periods of hundreds of nm (figure 9(b)). The formation of the crater shown in figure 9(b) is caused by laser beam refraction/reflection on the bubble. The ablation produces strong shockwaves, whose propagation imprints ripples on the smooth surfaces. As deduced from the inhomogeneous ripples on the fringe walls, the shape of shockwaves must be hemispherical rather than parallel, which has a much stronger central front. It will first cause surface melting followed by the side parts of the shockwaves. In light of the high amplitude of ablation shockwaves shown in figures 9(a)–(c), they must be the main reason for the principal cracking of grooves generated by laser ablation.

3.3.1.2. Bubble shockwaves. During laser ablation in water, two kinds of bubbles, cavitation bubbles (formed after ablation shockwaves) and bubbles formed due to water breakdown [16], are generated. No matter the bubble size, the bubble collapse will release shockwaves, whose amplitude is in the order of kPa [53], much lower than that of ablation shockwaves. Figures 9(d)–(f) give apparent evidence for tilt ablation caused by the beam refraction/refraction on small bubbles. Figure 9(d) shows the V-shaped microstructure obtained by fs-LSPAL at a scan speed of 1 mm s\(^{-1}\), which is obviously characterized by a U-shaped microstrip (figure 9(e)). Near the bottom of the V-shaped microstructure, a half-capped structure with a tail is observed (figure 9(f)), which indicates the occurrence of tilt ablation induced by the beam refraction/reflection by bubbles.

3.3.2. Crack nucleation, growth and propagation, and final rupture

3.3.2.1. Crack nucleation and powder dislocation: analysis based on the literature. When the pressure is in the range of 10–16 GPa, the phase transition of Si occurs, which renders the plasticity property to silicon [54]. Hence, plastic deformation involving a series of generation and transport of dislocations becomes possible.

The lattice defects (e.g. stacking faults and twinning) are the ‘hotbed’ for crystal dislocations under the compression of shockwaves [55]. During fs-LSPAL, a large number of grains with different crystalline orientations are produced [56]. Upon the impact of shockwaves at high temperature, grain boundary dislocation, migration [57], and spallation [58] of the crystals takes place, which lead to the dislocations of micro/nano-powders. Under high pressure or high temperature or their synergistic effects, it is possible that dislocation becomes activity in Si. The dislocation mobility of Si is \(2.60 \times 10^{-5}/\text{pa.s at } T = 850 \text{ K} [26]\), and the dislocation mobility increases exponentially with increasing temperature when T is above 850 K [59].

Shear stresses generated during laser ablation [60] cause the slip of crystalline grains, by which the facets of grains govern the slip orientation. Such a phenomenon is called deformation, from a mechanics perspective. The deformation bands can significantly concentrate the stresses, which can further trigger grain fracturing/splitting and grain spallation. The slip of many grains will spontaneously connect to form a long fracture, which will further propagate upon the successive impacts of the shockwaves.

3.3.2.2. Crack growth and final fracture: analysis based on experimental results. Due to a series of crystal slips and deformations induced under the impact of high-pressure

Figure 9. (a)–(c) Ablation shockwave traces on the crack surface obtained by fs-LSPAL at 700 mW and 1 mm s\(^{-1}\) with a 15 \(\mu\)m scanning interval. (a) Overview of an echelon fringe formed by fs-LSPAL. (b), (c) green and red areas in (a). (d)–(f) The structures indicating the presence of small bubbles, which resulted in refracted/reflective ablation. (d) A V-shaped crack structure generated by fs-LSPAL. (e), (f) Green and red areas in (d).
shockwaves during fs-LSPAL, small powders dislocate from the grooves (figures 6(a)–(i)). In consequence, a crack is initiated with the crack fronts propagating with an inclination angle of ~30° inside the grooves. The inclined crack propagation should be caused by the tilt ablation stemming from bubble reflection and refraction (figures 9(e) and (f)). During the propagation of an en échelon crack inside a groove, the crack fronts get arrested because of a reduction in the tensile stress or a sudden variation in the orientation of the tensile stress, which will cause the formation of microstructures (figures 2(a), (g), (j) and (m)). After cracking resumes, the stress property of the crack fronts is altered, so new fracture morphologies are generated. A series of arrests and resumptions of joint crack fronts leads to the formation of fringe-layer microstructures (figure 2(a)), which represent the shapes of crack fronts at the arrested moment. The propagation of microcracks is accompanied by the generation of nanocrack arrays, being the secondary cracks induced by a main crack inside the grooves (figures 2(f) and (i)). When the cracks reach to certain depths, their propagations will be oriented at a slant toward the top of the grooves. Further crack propagation is characterized by a series of arrest and resumption processes of crack fronts, leading to the formation of both curved microfringes and nanoripples on top of them (figures 2(n) and (o)). The main crack direction, that varies with the scanning direction, can be either from left to right or from right to left (figures 2(a) and (g)).

During micro- and nano-crack formation, strong shear pressures twist the crack fronts, while tensile stresses induce the opening and fluctuations of the structures so that the crack motions typically cause the opening (Mode I), sliding (Mode II), and scissoring (Model III) of the structures [46]. During fs-LSPAL, synergistic crack motions cause the formation of a curve (Modes I and II loading, continuous propagation, figure 2(a)), kink (Modes I and II loading, continuous propagation, figure 7(e)), gradual twist (Modes I and III loading, continuous propagation, striations in figure 3), and abrupt twist hackles (Modes I and III loading, discontinuous propagation, microscale layered fringes in figure 2(m)). The propagation path of the joint crack fronts is along the direction which minimizes the shear stresses and maximizes the tensile stress on the joint tip [46].

Kink structures are mainly generated by fs-LSPAL at a low speed of 0.2 mm s⁻¹ (figure 1(j)) and are seldom generated at higher speeds of 0.5 mm s⁻¹ and 1 mm s⁻¹ (figures 1(k) and (l)), which is attributed to stronger accumulated shockwaves impacting on the structures and more random ablation by reflected and refracted pulses at a low scan speed. Instead, fs-LSPAL, at a high scan speed of 1 mm s⁻¹, is good at inducing successive cracks featured by gradual twisted nanostriations. This means that changing the scan speed is a good approach to changing the crack modes and to manipulating the surface structures.

If two cracks occur simultaneously to the same place of one groove, the crack fronts will interfere with each other and lead to a strong binding of Wallner lines (figure 2(l)) and crack branching (figure 5). If nanocracks occur simultaneously or successively, the Wallner lines will interpose each other (figure 4(f)) and cause the ripple densification (figures 4(g)–(i)). Once multidirectional cracks form a semiloop (the critical crack size for unstable propagation) or a complete loop, the whole fracture area will become dislocated; and the crack lengths are as long as tens of μm (figures 2(a), (g), (j) and (m)).

3.4. Mechanism for restructuring HSFLs and pearl-necklace-like structures

Lattice defects and stacking faults are excellent nucleation sites for the initiation of amorphization upon shock compression [55]. The expansion of lattice defects and stacking faults along certain crystallographic orientations and intersects causes an increase in the amorphization rate [56].

The a-Si is also an indicator of surface melting [32], which contains both thermal and nonthermal modes [61]. In our experiments, through the analysis of surface morphologies, the surface melting/amorphization can also be divided into thermal and cold modes. Thermal melting/amorphization is characterized by the formation of long parallel ripples on the sidewalls of cracked surfaces (figure 7) induced by ablation shockwaves. The cold melting/amorphization is ascribed to the breaking of covalent bonds [61] and the formation of lattice defects and stacking faults [55] triggered by the gentle shockwaves stemming from bubble collapse.

During the cold melting, surface plasmon polaritons (SPPs) help carve the affected surface into HSFLs or pearl-like particles. The water environment is beneficial for the excitation of SPPs enabling the reduction of the periodicity of LIPSS into the range of 100–200 nm [48], which has been discussed in our previous work [32].

The occurrence of cold melting is also a result of a decrease in the melting point of Si with increases in the hydrostatic pressure [56]. For example, high pressures of 12–17 GPa can cause Si melting [62], which often occur at the grain boundaries [63, 64] and the lattice dislocations [65].

Under the impact of compressive shockwaves, the sidewalls of grooves can easily become cold melted when subjected to the impact of high-pressure shockwaves. Hence, selective formation of HSFLs is brought about, which mainly occurs in the X-Z plane of the broken grooves (see figures 7(a)–(h)) where the close spaces of broken grooves and the boundaries of protruding microstructures and the top parts of parabolic/elliptical ridges can efficiently block shockwaves. In the X-Y plane without structural barriers (open region of cracked structures), shockwaves can easily pass over without any surface restructuring.

At a lower scanning speed (i.e. 0.2 mm s⁻¹ vs. 0.5 and 1 mm s⁻¹), shockwaves can induce successive impacts on a larger area of surfaces in the X-Z plane so the densities of HSFLs and pearl-necklace-like particle arrays are much higher. As deduced from the formation of chaotic HSFLs and ejected particles, only on parabolic/elliptical ridges obtained at higher scan speeds of 0.5 mm s⁻¹ and 1 mm s⁻¹ (figures 7(m)–(p)), it is clearly seen that higher scan speeds induce a more liquid disturbance than a lower scan speed of 0.2 mm s⁻¹. This phenomenon is also verified in our previous report showing
that local liquid disturbance bends the orientation of UHSFLs on tungsten by fs-LAL in acetone [21].

4. Applications of the cracked structures formed by fs-LSPAL

4.1. Development of homogeneous macroporous structures

Cracking of the microgrooves during fs-LSPAL serves as a method to produce macroporous structures, but these structures are inhomogeneous (figure 1), which will limit their applications. To control the homogeneity of macropores by fs-LSPAL, the scanning line interval is narrowed to 5 \( \mu \text{m} \) at laser powers of 700 and 200 mW and scanning speeds of 0.2 mm s\(^{-1}\), 0.5 mm s\(^{-1}\), and 1 mm s\(^{-1}\). For 700 mW at 0.2 mm s\(^{-1}\), separated microstructures with lengths of 10–20 \( \mu \text{m} \) are produced (figure 10(a)) with a structure looking like a four-leaf clover (figure 10(d)) formed by random bubble-induced laser refraction/reflection during fs-LSPAL. At 0.5 mm s\(^{-1}\), long crack grooves with a length of more than 30 \( \mu \text{m} \) is well preserved (figure 10(b)), in which case most crack structures are characterized by HSFLs, unlike smooth structures generated at the scan interval of 15 \( \mu \text{m} \) (figure 1(c)). Thus, it can be concluded that a smaller scan interval facilitates the crack surfaces to be restructured into HSFLs. At 1 mm s\(^{-1}\), the structures turn out to be macroporous (figure 10(c)) with the macro pores oriented to different directions (figure 10(f)), very different from the vertical macro pores obtained at a larger scan interval of 15 \( \mu \text{m} \) (figures 1(a)–(f)) and those prepared by fs laser ablation in air [35, 37]. Crack structures can be found around the macro pores (figure 10(f)), which indicates the occurrence of microstructures induced by reflected/refracted laser ablation. While keeping the scan interval at 5 \( \mu \text{m} \), lowering the laser power to 200 mW allows more homogeneous surface structures to be prepared. Figure 10(g) shows the surface structures obtained at 0.2 mm s\(^{-1}\), consisting of tilt grooves of 2 \( \mu \text{m} \) in width fully decorated by HSFLs with periods of 100–200 \( \mu \text{m} \) (figure 10(j)). Increasing the scan speeds to 0.5 mm s\(^{-1}\) and 1 mm s\(^{-1}\) leads to the formation of more homogeneous macroporous structures (figures 10(h) and (i)) where en échelon cracks (figures 10(k) and (l)) can be easily identified.

To gain the 3D information about these cracked structures obtained by fs-LSPAL at 700 mW at scanning speeds of
Figure 11. (a)−(c), (h)−(j) Three-dimensional morphologies of surface structures obtained by fs-LSPAL at 700 mW at scanning speeds of 0.2 mm s$^{-1}$, 0.5 mm s$^{-1}$, and 1 mm s$^{-1}$ with scan intervals of 5 and 15 µm. (e)−(g), (k)−(m) Cross-sections of the structures marked by the red planes in (a)−(c), (h)−(j). (d) Two-dimensional morphology of the tilt macroporous structures obtained by fs-LSPAL at 700 mW and 1 mm s$^{-1}$ with a scan interval of 15 µm, providing additional information for the macropores shown in figure 10(c). (n)−(p), (q)−(s) Three-dimensional morphologies and cross-sections of structures obtained by fs-LSPAL at 200 mW at 0.2 mm s$^{-1}$, 0.5 mm s$^{-1}$, and 1 mm s$^{-1}$ with a fixed scan interval of 5 µm. Note that the red plane in (o) is at the rightmost, which cannot be distinguished.

0.2 mm s$^{-1}$, 0.5 mm s$^{-1}$, and 1 mm s$^{-1}$ with a scan interval of 5 µm, the as-prepared structures were characterized by a confocal microscope, as shown in figures 11(a)−(c). The cross-sections of structures marked by the red planes in figures 11(a)−(c) are displayed in figures 11(e)−(g). As seen, the cracks are not uniform with the microstructures characterized by different height fluctuations in different cases. At 0.2 mm s$^{-1}$, the highest height of the partially broken grooves is 51 µm, as shown in figures 11(a) and (e). At 0.5 mm s$^{-1}$, the maximum height of a partially broken groove which contains a sunken crater is 60 µm. But most microstructures are featured by green and blue colors (figure 11(f)) at a height of around 30 µm and 15 µm, as shown in figure 11(f). At 1 mm s$^{-1}$, except for one partial groove possessing a maximal height of 42.6 µm (figures 11(c) and (g)), most microstructures are not higher than 10 µm (figure 11(g)), providing the
3D information for the macroporous microstructures (figure 11(d)). The highest level of the tilt macropores shows the green color which corresponds to a height of 21 µm.

Figures 10(a)–(f) indicate that at a fixed laser power, fs-LSPAL, at the high scanning speed of 1 mm s⁻¹, can produce more homogeneous structures than at 0.2 mm s⁻¹, especially for macroporous structures. This reminds us to check the 3D structural morphologies and corresponding cross-sections of cracked structures generated by fs-LSPAL at 700 mW with a scanning interval of 15 µm at scanning speeds of 0.2 mm s⁻¹, 0.5 mm s⁻¹, and 1 mm s⁻¹, as shown in figures 11(h)–(j) and figures 11(k)–(m). At scanning speeds of 0.5 mm s⁻¹ and 1 mm s⁻¹, consecutive en échelon cracks cause the dislocation of most grooves during fs-LSPAL (figures 11(i) and (j)), so the structures are relatively homogenous with less height fluctuations (figures 11(l) and (m)). At 0.2 mm s⁻¹, only sparse en échelon cracks occur; and the grooves are less destroyed (figure 11(h)), as characterized by a frequent height fluctuation with the maximum height as high as 53 µm (figures 11(k)). Such a trend will be further verified by fs-LSPAL at the scanning interval of 10 µm for the purpose of examining their effect on cellular behaviors, which is shown in section 4.2.

Decreasing the laser power to 200 mW significantly reduces the heights of the as-prepared structures, with maximum heights of 33 µm, 19 µm, and 21 µm for 0.2 mm s⁻¹, 0.5 mm s⁻¹, and 1 mm s⁻¹, respectively (figures 11(n)–(s)). Meanwhile, the height fluctuations of surface structures are not so severe (figures 11(q)–(s)) as compared to the structures obtained at 700 mW. Compared to the surface structures produced at 0.2 mm s⁻¹, shown in figure 11(n), the structures obtained at 0.5 mm s⁻¹ and 1 mm s⁻¹ are more homogeneous (figures 11(o) and (p)), in accordance with the results shown in figures 10(h) and (i). The depths of the macropores are in the range of 4–6 µm. As mentioned above, because the sidewalls of the macropores may block the laser beam to gain the bottom information, the exact depths of macropores should be higher.

Many techniques have been utilized to develop macroporous Si structures, including acid etching [66], electrochemical etching [67], and photodarkening [68]. Compared with these acid-assisted methods, laser ablation offers a much more environmentally friendly method, although attempts to form macroporous structures are still limited [69]. Zhang et al prepared nanohole arrays (diameter: ~800 nm, width: ~300 nm) by fs laser ablation at different laser polarizations (100 fs, 850 nm, 1 kHz, 1 mm s⁻¹, air), which displayed vivid colors upon exposure to white light [35]. Yuan et al produced Si nanohole arrays with periods of 520–540 nm and depths of 100–200 nm by fs laser ablation in air (130 fs, 800 nm, 1 kHz, 300 m pulse⁻¹, 0.2 J cm⁻²), whose regularity strongly depended on scan speeds of 20–2000 µm s⁻¹ [34]. Ji et al found that multiple back-and-forth picosecond laser scanning was able to produce Si micropores with diameters of 25–30 µm, which possessed 6% reflectance in the visible to near-infrared range (wavelengths of 400–1000 nm) [36]. Most previous work was based on the back-and-forth scanning method with very low macropore productivity. Additionally, all previous work was performed in air and suffered from difficulty in forming deep macropores due to debris redeposition and material recasting in the pores [70]. At high laser powers or high fluences, a strong thermal effect takes place, even when using fs lasers [32], which increases the difficulty in controlling the surface morphology and may be risky for erasing macropores. This work demonstrates the possibility of producing both vertical (figure 1) and tilt (figure 10) macroporous structures via fs-LSPAL by changing laser powers and scanning speeds.

4.2. EB3 stem cell behaviours on cracked structures

To demonstrate the applications of cracked structures, EB3 stem cells were cultured on two samples obtained at fs-LSPAL at 700 mW, a scanning speed of 200 µm, and scanning intervals of 5 µm and 15 µm under the same culture conditions.
as described in section 2.2. Figures 12(a), (b) and (d), (e) show the cytoskeleton and nucleus of stained EB3 stem cells cultured on these two samples, which show that EB3 stem cells prefer to conglomorate into circular aggregates. Figures 12(c) and (f) display the representative stem cell colonies with sizes of 61 μm and 42 μm on each sample, respectively, from which it can easily be seen that each stem cell colony is composed of many small spherical stem cells several μm in size. Supported by the structural morphologies shown in figures 11(a) and (h), it can be concluded that height-fluctuated cracked structures can play the role of microwells [71, 72] to make stem cells aggregate inside. The cellular sizes are in a broad size range of 20–240 μm, with the majority in the range of 20–80 μm, with average values of 64 ± 38 μm and 55 ± 30 μm. In particular, the 700 m W-N-5 and 700 m W-N-15 samples excel at generating stem cell colonies in the size ranges of 40–60 μm and 20–40 μm. The structural inhomogeneity of cracked structures may affect the size distribution of stem cell colonies on both samples. Despite the challenge in controlling the crack process during fs-LSPAL, once realized it can be envisaged that different manners of crack structures can be used to culture different sizes of stem cells to study their size-related differentiation behaviors [71, 73].

5. Differences between fs-LSP and fs-LSPAL

Even though both fs-LSP and fs-LSPAL techniques utilize shockwaves to treat materials and liquids are sometimes used as the environment for fs-LSP, their purposes are different.

(1) Fs-LSP is often used to induce plastic deformation of the substrate materials, mainly aiming to improve the fatigue property of metallic materials. LSP-treated samples often need to be performed on a large scale to meet the requirements of fatigue measurements, which requires high laser powers (e.g. hundreds of μJ [74]) to generate a laser spot large enough to promise efficiency. Under such conditions, surface melting is inevitable so as to diversify the surface morphologies with random solidified molten layers, which is difficult to control. Meanwhile, there is no need to pay attention to these structures. Even though, in some cases, ordered surface structures like those produced by fs-LA are produced [75], they are not the main focus of LSP works.

(2) Fs-LSPAL mainly aims to upgrade the structuring capacity of laser ablation and enrich the diversity of the surface structures on brittle materials (e.g. Si, germanium (Ge), glass, etc.), never reported before this work. The applications of fs-LSPAL are expected to cover both the scopes of LSP and LAL. The spot size is very flexible and can be as small as several μm. The most important thing for fs-LSAL is to inhibit the thermal melting to initiate a ‘cold’ ablation, otherwise the structures will be erased by the molten layers.

(3) Water is frequently used for fs-LSP and fs-LSPAL. For the fs-LSP technique, it serves as a protective layer that can generate high pressures [75, 76]. With respect to fs-LSPAL, water not only brings about high pressure but also induces the formation of bubbles (cavitation bubbles, persistent bubbles, and free bubbles), which are seldom studied in the scope of fs-LSP. However, free bubbles play an important role in the surface structuring for fs-LSPAL. This work shows that tilt ablation induced by bubble reflection/refraction causes en échelon cracks of brittle Si grooves, leading to the formation of novel cracked hierarchical micro/nanostructures (figure 1) and homogeneous tilt macroporous hierarchical micro/nanostructures (figure 10) that cannot be achieved by the conventional LAL technique.

6. Conclusions

This work proves the feasibility of manufacturing novel macroporous hierarchical micro/nanostructures with the aid of shockwaves during fs-LSPAL, a novel manufacturing technique under extreme conditions. At a fixed scanning interval of 15 μm, the size of the macropores can be adjusted from 10 μm to 5 μm by changing the scan speeds. Upon the impact of ablation shockwaves, whose amplitudes are on the order of GPa, a series of slant cracks are excited with more than a 30° tilt angle from the top of the groove to its bottom under the synergistic impact of both shear stresses and tensile stresses. Once cracks reach the deepest regions (as deep as 12 μm), they will propagate upward to the top region. This process is accompanied by the arrest and branching of the crack fronts in different dimensions and directions, resulting in the formation of nano-scale parabolic/elliptical furrows and ridges and curved fringe-layered sidewalls. The periods of parabolic/elliptical ridges range from tens of nm to hundreds of nm, while the heights of fringe-layered sidewalls are on the submicron or micron scale, both of which are closely associated with the amplitude of local tensile/shear pressures. Consecutive cracking along the ablation path can be induced during fs-LSPAL at relatively higher speeds of 0.5 mm s⁻¹ and 1 mm s⁻¹. Striation is a ubiquitous phenomenon that occurs during fs-LSPAL, which produces stair-like nanolayers with heights normally less than 100 nm and as low as several nm, at minimum. The analysis of the partially broken grooves indicates that the spallation of submicron powders from the grooves is due to the expansion of cracks over a groove. After the crack network becomes semi- or completely looped, large pieces of powder, as long as 60 μm, are pelleted from the grooves, exposing the crack traces and crack structures. Based on surface structures imprinted on the fringe sidewalls by ablation shockwaves and the structures generated by tilt ablation due to the beam refraction/reflection by the bubble, the crucial roles of ablation shockwaves and bubble shockwaves for initiation of cracks and selective restructuring of HSFLs are deduced.

Through analysis of 3D morphologies of as-prepared structures, it is found that fs-LSPAL at the slow and high scanning speeds of 0.2 mm s⁻¹ and 1 mm s⁻¹ are good at generating height-fluctuated and height-homogeneous cracked structures. The high-fluctuated cracked structures can be used to induce ‘colony’ aggregate of EB3 stem cells like microwells.
Meanwhile, the feasibility of producing homogenous macroporous structures is also confirmed by fs-LSPAL at 700 mW and 200 mW at the high scanning speed of 1 mm s$^{-1}$ with a scanning interval of 5 μm. The homogeneous macroporous structures are composed of tilt microgrooves of ~20 μm in width oriented to different directions, whose formation is attributed to the refracted/reflected ablation induced by bubbles. Such tilt macroporous structures are achieved for the first time, so that it can be concluded that fs-LSPAL triggered simultaneous bubble refraction/reflection and that crack manufacturing is paving a new way for the generation of novel hierarchical macroporous structures. What is more, even the crack itself offers a new source for surface structuring. The striations allow the formation of layered structures with very high resolution of several nm, which are unachievable by laser ablation. The hierarchical structures obtained by fs-LSPAL are more uniform than natural crack-associated fractographic structures. However, this technique suffers from the drawback of limiting its wide application in practice.

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