Underwater persistent bubble-assisted femtosecond laser ablation for hierarchical micro/nanostructuring

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Received 16 December 2019, revised 27 January 2020
Accepted for publication 2 February 2020
Published 19 February 2020

Abstract

In this study, we demonstrate a technique termed underwater persistent bubble assisted femtosecond laser ablation in liquids (UPB-fs-LAL) that can greatly expand the boundaries of surface micro/nanostructuring through laser ablation because of its capability to create concentric circular macrostructures with millimeter-scale tails on silicon substrates. Long-tailed macrostructures are composed of layered fan-shaped (central angles of 45°–141°) hierarchical micro/nanostructures, which are produced by fan-shaped beams refracted at the mobile bubble interface (≥50° light tilt, referred to as the vertical incident direction) during UPB-fs-LAL line-by-line scanning. Marangoni flow generated during UPB-fs-LAL induces bubble movements. Fast scanning (e.g. 1 mm s\textsuperscript{-1}) allows a long bubble movement (as long as 2 mm), while slow scanning (e.g. 0.1 mm s\textsuperscript{-1}) prevents bubble movements. When persistent bubbles grow considerably (e.g. hundreds of microns in diameter) due to incubation effects, they become sticky and can cause both gas-phase and liquid-phase laser ablation in the central and peripheral regions of the persistent bubbles. This generates low/high/ultrahigh spatial frequency laser-induced periodic surface structures (LSFLs/HSFLs/UHSFLs) with periods of 550–900, 100–200, 40–100 nm, which produce complex hierarchical surface structures. A period of 40 nm, less than \frac{1}{25}\text{th} of the laser wavelength (1030 nm), is the finest laser-induced periodic surface structures (LIPSS) ever created on silicon. The NIR-MIR reflectance/transmittance of fan-shaped hierarchical structures obtained by UPB-fs-LAL at a small line interval (5 μm versus 10 μm) is extremely low, due to both their extremely high light trapping capacity and absorbance characteristics, which are results of the structures’ additional layers and much finer HSFLs. In the absence of persistent bubbles, only grooves covered with HSFLs with periods larger than 100 nm are produced, illustrating the unique attenuation abilities of laser properties (e.g. repetition rate, energy, incident angle, etc) by persistent bubbles with different curvatures. This research represents a straightforward and cost-effective approach to diversifying the achievable hierarchical micro/nanostructures for a multitude of applications.

Keywords: hierarchical micro/nanostructures, persistent bubble, femtosecond laser, surface structuring, beam refraction, fan-shaped microstructure, LIPSS
1. Introduction

Complex hierarchical micro/nanostructures are attracting increasing attention due to their unique interfacial properties and widespread applications [1–7]. As such, there is increasing demand for the exploration of novel and innovative techniques to diversify the hierarchical structures. Among all currently available techniques, laser ablation has a unique advantage: it is applicable to a wide variety of materials and is particularly well-suited to the hierarchical structuring of hard and chemically inert materials that are extremely difficult to process by conventional lithography techniques [8, 9]. Of the various environment mediums, including air, vacuum, gas and liquid, laser ablation in liquids (LAL) is the most attractive for both its single-step simultaneous construction of hierarchical micro/nanostructures [4, 7, 10–13] and its synthesis of nanocolloids [14–17] without releasing any hazardous pollutants (e.g. dust and toxic materials) into the atmosphere. During LAL, bubble formation occurs spontaneously, as a result of liquid decomposition and breakdown [15]. There are two kinds of bubbles: (i) cavitation bubbles [18], which normally collapse several microseconds after formation [19–21]; (ii) persistent bubbles [22], which are often generated by LAL in water [22]. Persistent bubbles can stay on the substrates for up to several minutes (as demonstrated in this study), and their emergence inevitably causes light scattering [23, 24], reflection [24] and refraction [24]. Thus, they are normally undesirable for bulk material cutting [25, 26] and nanomaterial synthesis [27]. However, to date, no attempt has been made to evaluate the advantage of utilizing persistent bubbles during LAL for surface structuring.

Persistent bubbles are typically superhydrophobic with contact angles over 150° [22]. The gas composition of persistent bubbles has been confirmed to be a mixture of oxygen and hydrogen, caused by the laser-induced decomposition of water molecules [22]. The refractive index of water is 1.33, while the refractive indices of gases, such as air, hydrogen and oxygen, are ~1. If a persistent bubble is large and robust enough to resist laser irradiation, the properties (repetition rate, energy, and direction) of the incident laser light must be attenuated at the bubble’s interfaces. From a geometric optics perspective, when a laser beam strikes the peripheral area of a large persistent bubble, it will be refracted [28]. Consequently, the ablation direction is no longer vertical as would be expected, but significantly tilted, as illustrated in figures 1(a) and (b) (front and side views) [28]. Due to the different curvatures of bubbles, fan-shaped ablation may occur during line-scanning LAL.

When a laser beam interacts with an underwater bubble, a temperature (surface tension) gradient develops beneath the bubble [29]. This induces a liquid motion, called Marangoni flow, the strength of which depends on the irradiation position of the bubble [28]. Generally, Marangoni flow would not be triggered in the area surrounding the bubble’s center and only a weak Marangoni flow can be initiated at the rim of a bubble. The strongest Marangoni flow is triggered near the center of a bubble [28]. Marangoni flows induced by the laser irradiation of a bubble have been applied as microfluidic pumps for liquid mixing [30], liquid filters for sorting polymer spheres of varying sizes [28], and as liquid templates for the self-assembly of nanoparticles [31, 32] and proteins [33]. Manipulating Marangoni flows generated from bubble movements induced by programmed laser irradiation even opens up the possibility of spatial nanopatterning [34, 35], nanoprinting [36, 37] and nanolithography [38]. Given that Marangoni flows are capable of propelling bubbles steadily, successive refracted laser ablation is expected to occur, as shown in figures 1(c)–(e) (front view of figure 1(c), side view of figure 1(d) and top view of figure 1(e)), which yields novel tailored fan-shaped microstructures.

In our previous research, we have successfully demonstrated that LAL can proficiently produce HSFLs with periods of 110–200 nm on silicon, on both the valleys and crests of microstructures. Hence, we can expect the hierarchical fan-shaped microstructures fully decorated by HSFLs to be generated by mobile-bubble-assisted femtosecond LAL [10]. Our current research addresses two main challenges facing HSFLs: (i) diversifying hierarchical micro/nanostructures covered by HSFLs and (ii) developing a technique that can yield finer LIPSSs, termed ultrahigh spatial frequency LIPSSs (UHSFLs), with sub-100 nm periods. Thus far, UHSFLs have been successfully developed on Ti [39–44], diamond-like carbon [45], nitrogen-doped diamond [46], and silicon [47, 48], with periods (λ) shorter than λ0/8. However, these UHSFLs can only be achieved at low fluences near ablation thresholds. Take silicon for example; the typical periods of Si- HSFLs are in the 120–220 nm range, approximately 0.15–0.275 times λ0, which can be easily achieved by fs-LAL, as reported in [10]. To date, the minimum period achieved with Si-LIPSSs is 70 nm (0.0875 × λ0, λ0 = 800 nm), which was obtained via fs laser ablation in oil at a repetition rate of 90 MHz [47]. In addition to MHz lasers, fs laser ablation in water at a repetition rate of 1 Hz can only produce Si-UHSFLs with a Λ of 80 nm (0.15 × λ0) at a fluence of 0.09 J cm−2 [48]. In contrast, the minimum Λ for Si-LIPSSs fabricated by most frequently used fs laser systems with kHz repetition rates is only 100 nm [48, 49], with a minimum Λ/λ0 ratio of ~1/10 (λ0 = 1045 nm) [10]. Hence, a technique that can enable the formation of UHSFLs with Λ < 70 nm and Λ/λ0 < 1/10 by kHz-lasers at higher fluences will revolutionize Si-UHSFL fabrication.

In our current research, in order to validate our conjecture shown in figure 1 and to develop UHSFLs with periods below 70 nm, underwater persistent bubble assisted fs-LAL (UPB-fs-LAL) of silicon was carried out at a laser fluence of 0.7 J cm−2. Special attention was paid to the correlation between as-prepared surface structures and bubble dynamics during both mobile and stationary-UPB-fs-LAL. Surface morphologies featuring tailored fan-shaped hierarchical micro/nanostructures, achieved through UPB-fs-LAL at a scanning speed of 1000 μm s−1 and a line interval of 5 μm, were selected as representative cases for detailed analyses. Surface morphologies generated by UPB-fs-LAL at scanning speeds of 100, 500 and 1000 μm s−1, and a line interval of 10 μm, were analyzed to demonstrate reproducibility and reveal morphological variations caused by processing/laser.
parameters. The polarization-dependent reflectance/transmittance of fan-shaped hierarchical micro/nanostructures, developed by mobile-UPB-fs-LAL, with scanning line intervals of 5 and 10 μm, at a fixed scanning speed of 1 mm s⁻¹, was measured for the purpose of conducting a detailed analysis to compare them to those obtained with an unpolarized beam. Finally, the perspectives on the advantages and disadvantages of this technique are discussed.

2. Experimental

An fs laser (CARBIDE, LIGHT CONVERSION, Vilnius, Lithuania) with a repetition rate of 200 kHz, a wavelength of 1030 nm, a pulse duration of 223 fs, and a laser power of 100 mW was used for UPB-fs-LAL. The pulse energy was calculated as 0.5 μJ. The laser spot size focused on the substrate surface using a 20× objective lens (numerical aperture (NA) = 0.4, Mitutoyo, Kawasaki, Japan) was 13 μm. The laser fluence was calculated as 0.75 J cm⁻². A single crystalline p-type (100) silicon substrate (20 × 15 × 1 mm) was placed inside a glass culture dish filled with 8 ml of distilled water, which had a liquid thickness of 5 mm. Scanning areas of 2 × 2 mm were ablated with a scanning line interval of 5 μm, at a scanning speed of 1 mm s⁻¹ and scanning line interval of 10 μm, as well as at scanning speeds of 0.1, 0.5, and 1 mm s⁻¹ using the line-by-line scanning method described in [50]. A CCD camera was used to monitor and record the ablation processes from the top. Scanning electron microscopy (SEM) (Thermo Fisher Scientific, Quattro ESEM, Tokyo, Japan) was used to characterize the surface structures. Schematics of different ablation scenarios were drawn by the software Paint 3D. The periods of the formed structures were measured by the software ImageJ. The optical properties of the ablated surface structures were analyzed by Fourier-transform infrared spectroscopy (FTIR) spectroscopy (FT/IR-6300, JASCO).

3. Results and discussion

3.1. Tailed concentric-circle macrostructures obtained by UPB-fs-LAL

3.1.1. Correlation between bubble dynamics and macroscopic structures. To demonstrate the dynamics of persistent bubbles, we first analyzed the bubble states at the beginning of the UPB-fs-LAL process. Figures 2(a)–(c) illustrate the bubble dynamics during the 1st and 2nd line scans of fs-LAL. Before the UPB-fs-LAL process began, the target surface was clean and free of any bubbles (figure 2(a)). Then when UPB-fs-LAL was initiated, many small bubbles were generated while scanning the 1st line (figure 2(b)), some of which remained on the target surface and became persistent bubbles. The size of the bubbles in figure 2(b) ranged from 7 to 46 μm in diameters, with 24 μm as the average. During the 2nd line scan, one persistent bubble already increased to 270 μm. Figure 2(f) illustrates the initial bubble generation (figure 2(d)), the subsequent bubble enlargement (figure 2(e)), and the formation of a large persistent bubble during UPB-fs-LAL, as part of our experimental observations. Then, UPB-fs-LAL was initiated. As fs-LAL proceeds, persistent bubbles grow by continuously absorbing newly formed small bubbles. This is known as the incubation effect, which can lead to a six-fold or greater enlargement in bubble volume [51], up to the submillimeter scale [22, 52]. Figures 2(h)–(j) demonstrate the dynamics of the same persistent bubble responsible for the formation of the tailed and concentric-circle macrostructures of bubbles with diameters of 220, 370 and 660 μm, respectively. Regardless of bubble size, bubble-induced light refraction always occurred, as indicated by the small green arrows in figures 2(h) and (i). When the laser beam reached a close proximity to the persistent bubble, the bubble moved downward, as indicated by the variation in bubble position relative to the green line (figure 2(i)). Refracted fs-LAL with gradually growing bubbles generated the tailed macrostructure shown in figure 2(g). The light and dark contrast regions in figure 2(g) correspond to ablated and unablated regions, respectively, as indicated by the dark areas outside the 4 mm².
Figure 2. (a)–(c) Optical images of persistent bubbles generated during UPB-fs-LAL using a line-by-line scanning method. (a) The initial state of the substrate without laser ablation. Scanning directions from left to right and top to bottom are shown in (a) by arrows. Formation of (b) small bubbles during the 1st lateral line scan and (c) larger bubbles during the 2nd lateral line scan due to the bubble incubation effect. The laser spots are marked by green circles in (b), (c). (d)–(f) Schematics showing the size increase of a persistent bubble as UPB-fs-LAL proceeds. (d) Small bubbles are generated at the beginning of UPB-fs-LAL, some of which stay on the substrate to become persistent bubbles. (e) The persistent bubble grow by absorbing small bubbles generated by subsequent pulses. (f) Further increase in the size of a persistent bubble, which starts to affect the pulses that cause UPB-fs-LAL. The scale bar in (a) is 100 μm. (a)–(c) Have the same magnification. (g) SEM image of the 2 × 2 mm ablated area (scale bar: 1 mm). (h)–(j) Optical images showing the bubble dynamics for the formation of the tangled macroscopic structure. (h) Bubble dynamics when the persistent bubble is small. The small green arrows indicate the refraction of the laser beam when it passes through the persistent bubble. (i) Bubble mobility when the laser passes the persistent bubble. The green line in the left image in (i) indicates the original position of the persistent bubble, while the lower bubble positions in the middle and right images in (i) indicate the bubble movement induced by Marangoni flows. The laser spots in (i) are encapsulated in green circles. The large green arrows in (h) and (i) show the bubble dynamics in time sequence. (j) Optical images showing different laser states as the laser beam passes through a large sticky persistent bubble, which leads to the formation of macroscopic concentric structures. The centers of the green circles are the positions where the laser hit the bubble. Small bubbles formed beneath the large sticky bubbles are indicated by black arrows. The scale bar in (h), which corresponds to 100 μm, applies to the images in (i) and (h)–(i) as well. Ablation conditions are as follows. Pulse duration: 223 fs, wavelength: 1030 nm, pulse energy: 0.5 μJ, repetition rate: 200 kHz, scanning speed: 1 mm s⁻¹, line interval: 5 μm.

scanned range, illustrated by the white arrow in figure 2(g). Thus, the scenario proposed in figure 1 was experimentally validated in this study. When the persistent bubble grew large enough in size (diameter: 660 μm), it stuck to the substrate surface.

Previous reports have stated that if persistent bubbles remain in the beam path, they will greatly affect the ablation state and induce side effects, such as deviations from the intended beam path [10, 53], beam splitting that will result in double-line ablation [25, 26], and inefficient ablation due to the beam blocking effect, leaving the surface unstructured [53]. In our study, strong light scattering occurred when the laser beam passed through the central area of a large persistent bubble, as signified by the appearance of dense white scattered dots (1st image in figure 2(j)). No strong scattering was observed when the beam passed through the peripheries (other images in figure 2(j)). Instead, light refraction became more significant (2nd and 3rd inset in figure 2(j)), as indicated by the appearance of white speckles at the rim of the persistent bubble. In certain sections of the persistent bubble, only refraction light was observed (3rd image in figure 2(j)); in other sections, neither refracted light nor laser spots were detected (4th image in figure 2(j)). Small persistent bubbles were formed right below the large persistent bubble, as indicated by the black arrows in the 5th image in figure 2(j), indicating that some refracted pulses ablated the area beneath the large persistent bubble. This is corroborated by the last image in figure 2(j), where a new small persistent bubble was generated between two existing small bubbles. Hence, it is evident that bubble dynamics
Figure 3. (a) SEM image of a tailed concentric-circle macrostructure obtained by UPB-fs-LAL. (b) Enlarged SEM image of the concentric macrostructure in (a), divided up into four regions (region 1: the almost unablated central area; region 2: the ring surrounding region 1; region 3: rim of region 2, where many small unablated circular islands were created; region 4: the unablated outermost area). (c) A blowup of the lower rectangle in (b), showing the small unablated circular islands in region 3. Scale bars in (a), (b), and (c) are 1000, 400, and 100 μm, respectively. (d)–(f) Schematics of the persistent bubble dynamics in regions 1, 2, 3, and 4, respectively. (g) Schematic of regions 2 and 3 where refracted laser ablation in region 2 generated small persistent bubbles in region 3. (h) Cross-sectional view of UPB-fs-LAL and corresponding light states in regions 1–4. The incident pulses are represented by red solid circles, while the attenuated refracted and scattered/reflected pulses are indicated by black and blue solid circles, respectively. Contact angle (CA) of persistent bubble is calculated to be 162°. (i) Blowup of upper rectangle in (b). (j) Blowup of the tailed macrostructure in (a). (k) Schematic of the formation scenario of tailed macrostructure by mobile-UPB-fs-LAL. Scale bars in (i) and (j) are 50 and 200 μm, respectively.

become extremely complex when the laser passes through a large stationary persistent bubble. Therefore, from the macroscale to the nanoscale, the structures obtained by stationary-UPB-fs-LAL can be expected to greatly vary from those obtained by mobile-UPB-fs-LAL or by LAL in the absence of persistent bubbles.

A magnification of the tailed concentric-circle macrostructure in the central region of figure 2(g) is shown in figure 3(a). The two horizontal unablated strips near the tailed macroscopic structure (see two horizontal black lines in figure 3(a)) were formed as a result of the blocking effect induced by the two nearby persistent bubbles, and their subsequent collapse, as UPB-fs-LAL proceeded. The concentric-circle macrostructure is divided up into four regions, as displayed in figure 3(b), demarcated by the surface morphologies obtained at different bubble positions, which will be discussed in detail below.

The circular central region (region 1) with a diameter of 200 μm was largely unablated due to an extremely strong light scattering effect (1st inset in figures 2(j) and 3(d)). Region 1 was surrounded by a ring-shaped macrostructure with a width of 70 μm, forming region 2. At the rim of region 2, multiple unablated circular islands with diameters of 20–36 μm were created (figure 3(c)), composing region 3. The appearance of these unablated small circular islands indicates that in addition to large persistent bubbles, small persistent bubbles are also present, and are anchored in the spaces between the large bubble and their underlying target surfaces (figure 3(g)), as depicted in figure 2(j). The small bubbles remained beneath the large persistent bubble, which caused strong light blocking. The outermost circular region (region 4) was unablated due to strong light blocking (reflection) by the large persistent bubble (figure 3(h)).

The bubble dynamics of UPB-fs-LAL is similar to the Marangoni flows triggered by fs laser irradiation that occur at different positions of a microscopic bubble [28]. No Marangoni flow was observed in region 1. However, significant Marangoni flow was exhibited in regions 2 and 3, though the effect decreased near the rim of the bubble (region 4). Marangoni flows are thought to be induced by the light reflection and refraction occurring during laser irradiation of the bubble at different positions [28]. As successfully demonstrated by our experimental results as well as past research [25], we can conclude that successive refraction of the laser beam occurs at the two liquid-gas interfaces located at both the top and bottom of bubbles in certain regions of a
large persistent bubble (figure 3(h), black arrow); otherwise, the whole area beneath the persistent bubble, including region 4, would be completely ablated. Light scattering [54], direct light reflection at the bubble interface, and refraction followed by subsequent reflection inside the persistent bubbles [24] dominate regions 2–4 during laser irradiation of the bubbles (figure 3(b), blue lines). Given the similarity between regions 1 and 4, region 4 is not separately analyzed.

The unablated central region is the contact area where the large persistent bubble anchors onto the substrate. The contact angle (CA) of the bubble is estimated to be 162°, as calculated by the expression $180°-\arcsin(R_{1st\text{-}area}/R_{bubble})$, where $R_{1st\text{-}area}$ and $R_{bubble}$ represent the radius of the first area (∼110 μm) and the radius of the persistent bubble (∼330 μm), respectively (see figure 3(h)). The persistent bubbles were determined as superhydrophobic, which is in line with the findings of a past report [22].

Figure 3(i) exhibits the uppermost section of the concentric-circle macrostructure, where no small-bubble-induced structures like those in figure 3(c) are found, which indicates that when a persistent bubble becomes sticky, the majority of small bubbles generated during stationary-UPB-fs-LAL will be absorbed by the large persistent bubble rather than remain on the substrate. Figure 3(j) illustrates the magnified tilted macrostructure obtained by mobile-UPB-fs-LAL (figure 3(k)), which is distinct from any microstructures ever produced by laser ablation of silicon in liquids without persistent bubbles [10, 55, 56], as well as from those produced by stationary-UPB-fs-LAL (figure 3(b)). The tilted macrostructures will be analyzed in section 3.1.2, followed by a detailed analysis in section 3.1.3, depicting the micro/nanostructures obtained from the 1st to 3rd regions of the concentric-circle macrostructure.

### 3.1.2. Tailed macrostructure: hierarchical layered fan-shaped micro/nanostructures

Figure 4(a) shows enlarged SEM images of tailed macrostructures, which consist of hierarchical layered fan-shaped micro/nanostructures, as designed in figure 1(e). Each fan-shaped layer is composed of microgrooves with lengths of 2–10 μm and widths of 4–7 μm, as well as microwells with hole diameters of 1–4 μm (figure 4(a)). Figures 4(b), (g) and (h) display enlarged SEM images of fan-shaped structures with disparate central angles. The central angle of the microgrooves in figure 4(b) is approximately 90°, where ablation occurred upward. The central angles of the microgrooves to the left and right of the fan-shaped macrostructure in figures 4(g) and (h) are 141° and 45°, respectively. Note that the fan-shaped microstructures are not perfectly symmetric (figures 4(g) and (h)), which indicates the varying states of the refracted pulses.

As a result of severe light refraction induced by the bubble interface (figures 1(a) and (b)), the ablation direction was no longer perpendicular to the substrates [10]. Hence, the microwells were still shadowed by the microprotrusions (figures 4(a), (b) and (g), (h)) even though the images were taken at a tilted angle of 20°. Figures 4(c)–(f) and (i)–(l) reveal enlarged SEM images of nanostructures formed on the sidewalls of microgrooves with varying central angles. Multitudes of sparse nanoprotrusions with diameters of 30–170 nm and heights of 50–270 nm were observed (figures 4(d), (i), and (k)). These nanostructures formed as a result of the spallation of molten droplets from the substrates [57]. Only two obscure LIPSSs, 74 and 100 nm in width, were observed in the deepest section of the ablated cavity (figure 4(e)), while in the open crater nearby (open rectangle 3 in figures 4(c), (f)), additional LIPSSs were found. The periods of LIPSSs ranged from 50 to 230 nm, i.e. roughly $\lambda_0/50–\lambda_0/5$, which demonstrated the feasibility of UHSFL fabrication by mobile-UPB-fs-LAL. Figures 4(c)–(f) also signify that LIPSSs do not readily form on the side walls of grooves during mobile-UPB-fs-LAL, but are much easier to fabricate at crater edges. Observation with a tilt angle of 50° demonstrated a flat arrangement of fan-shaped structures with different central angles (figures 4(m)–(o)), which indicate that bubble refraction caused a ∼50° tilt in the vertically incident laser beam.

### 3.1.3. Concentric-circle macrostructure: LSFLs/HSFLs/ UHSFLs

Figure 5(a) is a higher-magnification SEM image of region 1, as first illustrated in figure 3(b). As depicted, many sparse ablated areas (bright-colored areas) with sizes of 2–20 μm were produced. These areas had distinct sizes and morphologies, indicating a random modulation of pulses by the stationary persistent bubble. Figure 5(b) is a high-magnification image of the area enclosed within rectangle 1 in figure 5(a), displaying two incomplete and one fine Si-LSFLs, indicated by the three arrows. Figure 5(c) shows the enlarged morphology of the fine LSFLs in figure 5(b), which have periods in the 550–900 nm range, approximately 0.53–0.87 times $\lambda_0$ ($\lambda_0 = 1030$ nm). The orientations of LSFLs are perpendicular to the direction of laser polarization. The crest surfaces of the fine LSFL are decorated with particles that have a broad size distribution of 2–90 nm (figure 5(d)). Near the Si-LSFLs, HSFLs with periods of 150–230 nm were discovered (dashed rectangle in figure 5(b), inset is the enlarged image), which suggest that the pulse energy was greatly attenuated by the persistent bubble. Besides bubble shielding, optical breakdown and beam filamentation [58] may also occur, which could synergistically reduce the pulse energy and pulse number for laser ablation. Far from the LSFLs, in the area enclosed within rectangle 2 in figure 5(a), HSFLs were formed as well, whose comprehensive view and close-up are presented in figures 5(e) and (f), respectively. The periods of HSFLs are in the 100–250 nm range, with the ratio $\lambda_0/10–\lambda_0/5$. Simultaneous formation of both HSFLs and LSFLs signifies the attenuation of pulse energy or repetition rate by the persistent bubble (figure 3(h)), since HSFL can only be only achieved by fs laser ablation at lower fluences and repetition rates [59].

To demonstrate the differences between LIPSSs obtained by fs-LAL in the presence and absence of persistent bubbles, the grooves in the uppermost region of the 2 × 2 mm ablated
Figure 4. (a) SEM image of the fan-shaped hierarchical micro/nanostructures, a blowup of the SEM image of the tailed macrostructure in figure 3(i). (b) Enlarged SEM image of the central area, where the laser scanning direction was upward. The direction of laser polarization is shown in (b). (c) Enlarged SEM image of the craters shown in (b). (d)–(l) SEM images of the regions delineated by squares 1–3 in (c). (m) SEM images of fan-shaped microstructures with different central angles, respectively. (i), (k) Enlarged SEM images of the microstructures shown in (g), (h). (i), (l) SEM images of the nanostructures in open rectangles in (i), (k), respectively. (a)–(o) Images were taken at tilt angles of 20° and 50°, respectively. The scale bars in (a)–(l) are 50, 20, 4, 0.5, 0.5, 20, 4, 0.5, 4, 0.5, 50, 20 and 20 μm, respectively.

Figure 5. (a) Overview of the structures obtained in region 1, as labeled in figure 3(b). (b) SEM image of LSFLs and HSFLs enclosed within rectangle 1 in (a). (c) Enlarged SEM image of the fine LSFL with a period of 550–900 nm shown in (b). (d) Further enlarged SEM image of LSFL where many particles are clearly seen on top of ripples. (e) SEM image of HSFL structures inside rectangle 2 in (a). (f) Enlarged SEM image of HSFL structures shown in (e). (g) SEM image of structures inside rectangle 3 in (a). (h) SEM image of HSFL and UHSFL structures inside rectangle 1 in (g). (i) SEM image of HSFL structures inside rectangle in (h). (j) SEM image of HSFL and UHSFL structures inside rectangle 2 in (g). (k), (l) SEM images of UHSFL structures in the left and right rectangles in (j), respectively. Scale bars shown in (a)–(l) are 50, 1 (inset in b enlarged from the dashed rectangle)/10, 3, 0.5, 5, 0.5, 10, 1, 0.4, 1, 0.4, and 0.4 μm, respectively. The directions of light polarization are indicated in (b) and (c).
area, achieved via fs-LAL in the absence of persistent bubbles, were characterized (see figure 6). As shown, the grooves were much deeper than those in the ablated regions, which were obtained by UPB-fs-LAL (figure 5(a)), demonstrating that pulse energy was significantly reduced by the large persistent bubble, due to the strong light scattering effect (figure 2(j)). The two deeper strips (figure 6(b)) in the ablated groove arose as a result of the presence of cavitation bubbles, rather than persistent bubbles [25]. Only HSFLs with periods of 100–200 nm were observed in different sections of the grooves (figures 6(d)–(f)); rectangles 2–4 in figures 6(a), (c); rectangular region in figure 6(b)), which is in line with our previous study [10]. Interestingly, HSFLs obtained by fs-LAL in the presence (figure 5(f)) and absence (figures 6(b)–(f)) of persistent bubbles differed in the following three respects: (1) HSFLs in figure 6(f) are not continuous with multiple breaks, which is unlike typical HSFLs (figures 6(b)–(f)) obtained in the absence of persistent bubbles. (2) Rough protrusions narrower than the widths of HSFLs appear on the crests of HSFLs (figure 5(f)). Thus, the surfaces of the ripples are not as smooth as those previously achieved [10]. (3) Countless particles with sizes ranging from tens of nm to 200 nm were deposited on the unablated surface surrounding the crater (figures 5(c) and (e)).

Considering the fact that Si-LSFLs (figures 5(c) and (d)) are generally formed in a gas, it is reasonable to conclude that laser ablation in the central region of a large persistent bubble (which may contain oxygen, hydrogen and dissolved air [22]) is equivalent to laser ablation in a gas (region 1 in figure 3(d)). The surface roughness of HSFLs/LSFLs and the particles around the craters both stemmed from particle deposition within the persistent bubble. Additionally, though a 200 kHz pulsed laser was used, only limited pulses could pass through the central region of the persistent bubble to induce the formation of HSFLs and LSFLs. Were that not the case, the central region would have been ablated completely, rather than only sporadically. Thus far, for laser ablation in air, only fs lasers at MHz have been reported as suitable for inducing the formation of HSFLs with periods of 110–160 nm on silicon [60]. However, in this experiment, we demonstrated the novel feasibility of producing, in a gas environment, Si-HSFLs with periods of 100–250 nm (just like those obtained by LAL [10]) through stationary-UPB-fs-LAL.

Figure 5(g) details the morphology of rectangle 3 in figure 5(a), where both HSFLs and UHSFLs are found, as outlined by the enlarged SEM images (figures 5(h) and (j)) of rectangles 1 and 2 in figure 5(g), respectively. UHSFLs were more compact than HSFLs, with almost no space between the ripples. UHSFLs were generated at the rims of craters, whereas HSFLs were produced in the central region of craters. Moving from left to right within the central region, the periods gradually increased from 65 to 105 nm (figure 5(k)). The periods of UHSFLs were in the 55–93 nm range, i.e. roughly λ/20–λ/10, as shown in figures 5(i), (k) and (I), respectively. Figure 5(l) displays multiple separated nanogrooves consisting of UHSFLs, with lengths of 600–850 nm and widths of 37–65 nm, which could be the precursors of UHSFLs. The observation of coarse HSFLs (figure 5(j)) near UHSFLs indicates that both structures were produced in a gas environment. Thus, we also demonstrated the ability to develop Si-UHSFLs with periods of 55–100 nm in a gas environment during stationary-UPB-fs-LAL.

Figure 7(a) features the surface morphology of the region labeled 2 in figure 3(b). The strips labeled 1–3 all revealed differing visual appearances during SEM observations. Figure 7(b) illustrates the enlarged structural morphology of the larger rectangle in figure 7(a), where both HSFLs and UHSFLs were observed, their boundaries outlined in black. The overview morphologies of HSFLs and UHSFLs are displayed in figures 7(c) and (d), respectively. The periods of HSFLs and UHSFLs were in the ranges of 100–200 and 50–100 nm, respectively. Magnified images are shown in figures 7(e) and (f). 50 nm (figure 7(f)) is the smallest period ever obtained for a Si-LIPSS [10]. The period/wavelength

Figure 6. (a) SEM image of the groove obtained in the uppermost region of the 2 × 2 mm ablated area in absence of persistent bubbles. (b) Enlarged SEM image of rectangle 1 in (a). (c) Enlarged SEM image of rectangle in (b). (d)–(f) SEM images of rectangles 2–4 in (a). The direction of light polarization is indicated in (a). Scale bars in (a)–(f) are 10, 2, 0.5, 0.5, 0.5 and 0.5 μm, respectively.
ratio is 0.049, i.e. less than $\lambda_0/20$, which is also the smallest period/wavelength value obtained to date for a Si-LIPSS. The smooth surfaces of the HSFLs (figures 7(e) and (f)) indicated that laser ablation occurred in water, rather than in gas. Therefore, in addition to establishing the ability to generate UHSFLs in a gas environment (figures 5(g)–(l)), we also demonstrated the possibility of generating UHSFLs in water. Figure 7(g) reveals the surface morphology of UHSFLs formed inside the smaller rectangle outlined in figure 7(a), where UHSFLs are found between the unablated regions and HSFLs, as identified by the white arrows. These UHSFLs were located at the boundary of the arc-like structure that was presumably generated by small persistent bubble assisted fs-LAL.

Figure 7(h) displays the nanostructures present at region 3 of figure 3(b), which were produced by both large-
small-bubble assisted fs-LAL. As depicted, the unablated region was not perfectly circular and contained a few corrugated edges where a couple of UHSFLs were found. No ablation in the central region of figure 7(h) could be deduced from figures 7(i) and (m) (red rectangle in figure 7(h), magnified), which exhibited no trace of LIPSSs, only small and large deposited particles instead. These particles emerged during laser ablation [10, 15–17], which were impeccably deposited around the centers of the persistent bubbles. Figure 7(i) shows the surface morphology of the green rectangular area in figure 7(h); UHSFLs were found in the area outlined in black. As expected, UHSFLs were generated at the rim of the small persistent bubbles during stationary-UPB-fs-LAL. Figures 7(j) and (k) reveal enlarged images of the red and green rectangles in figure 7(i), which demonstrate that the periods of ripples increase radially, from the unablated area to the outer ablated area (as indicated by the arrow in figure 7(j)). The period of the leftmost ripple in figure 7(j) was 80 nm, which increased to 83 and 90 nm for the 2nd and 3rd ripples from the left, and was further lengthened to 110 nm as the ripple continued radially outward. The periods ultimately reached 150–200 nm (figure 7(k)). The formation of HSFLs is thought to be due to the modulation effects of molten layers [10] by surface plasmon polaritons (SPP) [48] or second-harmonic generation (SHG) [61]. It is noteworthy that liquid environment such as water significantly influences the periodicity of the excited SPPs after phase alteration and resolidication of ablated materials [48], resulting in the reduction of periodicity of LIPSSs, as thoroughly summarized in [10].

The surfaces for HSFL and UHSFL formation were presumed to be in moderate to gentle molten states, resulting from relatively higher and lower fluences. This speculation is based on the radial formation of HSFLs near the LSFL region, from the center of the laser to the outermost region on ZnO, induced by laser ablation in air [62]. This prompted us to check the position of Si-UHSFLs generated by fs-LAL at 1 Hz [48]. UHSFLs were only found at the rim of the ablated crater, while a large area of LSFLs was found in the central region, similar to the observed trend. In our case, only a limited region within the small persistent bubble was able to lower the pulse energy to values suitable for HSFL formation. Thus, UHSFLs can only be generated in a very limited area (figure 7(j)).

In regards to the formation of large areas of UHSFLs sandwiched between the HSFL regions illustrated in figure 7(a), they can be attributed to the formation of numerous structures similar to those displayed in figure 7(b). The small persistent bubbles beneath the large persistent bubble in region 2 could have been mobile during UBP-fs-LAL, which would have caused a continuous formation of UHSFLs, eventually resulting in the UHSFLs strips shown in figure 7(a). Analysis of the structures shown in regions 1, 2 and 3 of figure 3(b) reveals that disparate regions of the large persistent bubble attenuate the incoming pulses differently. The small persistent bubbles beneath the large bubble cause further attenuation. These reactions lead to the formation of micro/nanostructures with varying morphologies. The space between the big persistent bubbles and their anchored substrates, which contain extremely thin liquid layers with thicknesses of tens of microns, creates a special local environment that offer unique features not achievable via ablation in open, thick liquid environments [63], such as bubble dynamics and bubble-modulated pulse states that are distinctive in terms of energy, repetition rate and beam size.

3.2. Effect of laser/processing parameters on tailed macrostructures

To demonstrate the effects of laser/processing parameters on the formation of tailed macrostructures and concentric-circle macrostructures, experiments were performed by UPB-fs-LAL at varying scanning speeds of 1, 0.5 and 0.1 mm s⁻¹ at a line interval of 10 μm, while keeping other parameters constant (223 fs, 1030 nm, 0.5 μJ, and 200 kHz). As displayed in figure 9(a), at a scanning speed of 1 mm s⁻¹, the rightmost tailed structure stretched to 2 mm. In addition to generating the longest tailed region, two other tailed macrostructures were produced as well (figure 8(a)). The one on the left was separated by an unablated strip, presumably owing to the bubble breakdown that occurred there. The one in the middle obtained a large unablated circular region with a diameter of ~740 μm, likely due to the fact that the large persistent bubble became stuck there. Within that circular region, the ablated spots and lines were sparse. This conveys that when the bubble becomes too large, it can induce strong surface scattering and reflection, which in turn greatly reduces the ablation rate near the center. Surprisingly, at a fixed line interval of 10 μm, lowering the scanning speed to 0.5 mm s⁻¹ shortened the tail length to around 1 mm and diminished the diameter of the circular region to 480–530 μm (figure 8(b)). When the scanning speed was further decreased to 0.1 mm s⁻¹, spherical regions with diameters of 320–350 μm were generated and no tailed structures were found (figure 8(c)).

Figures 8(a)–(c) exhibit that faster scanning yields longer tailed macrostructures. The longer tail is partially the outcome of lower incubation rates of bubble sizes during faster UPB-fs-LAL. At lower scanning speeds, i.e. when there are more pulses incident to per area during ablation, the driving force for a Marangoni flow, and the resulting tail, is expected to be much stronger. However, our experimental results show the opposite, presumably due to the differing mobilities of the three triple-phase liquid-bubble-substrate contact lines of the persistent bubbles that occur during UPB-fs-LAL at different scanning speeds. Rapid speed scanning allows long-distance bending of the liquid-bubble-substrate triple contact line as it is driven downward by the Marangoni flow, as indicated by the undulating green line in the inset of figure 8(a), so that the bubble can be pushed downward much easily (see figure 2(i)). Contrarily, slower scanning (0.5 mm s⁻¹) only allow local bending of the contact line, while scanning at the lowest speed (0.1 mm s⁻¹) only allow spot bending of the contact line, which causes difficulty in pushing the bubble steadily downward. Moreover, lowering the scanning speed also increases the collapse rate of persistent bubbles, as evidenced
by the increasing number of unablated islands in figures 8(a)–(c), which could be another reason behind the formation of the largest persistent bubble at a scanning speed of 1 mm s⁻¹.

To avoid duplicate analyzes of similar structures, the longest tailed macrostructure is chosen as a representative case in the subsequent sections to demonstrate the reproducibility of UPB-fs-LAL for novel structure preparation under various conditions.

### 3.2.1. Fan-shaped hierarchical micro/nanostructures

Figures 9(a)–(g) illustrate the bubble dynamics throughout the formation of the longest tailed macrostructure (figures 8(a) and 9(m)) during UPB-fs-LAL at a scanning speed of 1 mm s⁻¹ and a line interval of 10 μm. First, two small persistent bubbles, both with diameters of 175 μm, were formed (figure 9(a)). These then coalesced into a single larger persistent bubble with a diameter of 230 μm (figure 9(b)). As the laser scanning continued, the persistent bubble grew, reaching 286 μm in diameter (figure 9(c)). Figures 9(d)–(i) depict the morphologies of this particular bubble as UPB-fs-LAL proceeded. The laser beams appear as white spots on the bubbles, close to the blue lines. When the incident laser progressed closer to the center (figure 9(d)) of a persistent bubble (diameter: 317 μm), the Marangoni flow compressed the bubbles, as displayed by the elongated white central region of the bubble. Thus, the bubble was pushed downward (figure 9(e)), as in line with the contact line analysis shown in the inset of figure 9(a). The laser light underwent strong refraction when passing through the persistent bubble, as demonstrated by the large white spots on the outermost region of the bubble (figures 9(e)–(f)). Since the persistent bubble is located at the rightmost side of the 2 × 2 mm scanning area, where the scanning direction shifted with stage deceleration/acceleration, the underlying substrate was subjected to a longer period of ablation by the refracted laser (figure 9(g)). Therefore, much deeper radical structures with central angles of 37°–64° and lengths of 40–60 μm were produced (figure 9(n)). When the laser beam moved leftward, the bubble was pushed further downwards, as evidenced by the distorted bubble relative to the blue lines (see figures 9(h) and (i)). When the bubble size increased to ~400 μm, Marangoni-flow-driven bubble movement arose, as exhibited by figures 9(j)–(l). Due to the magnitude of the persistent bubble, step-by-step movement could be identified when the laser beam passed through the center of the bubble, as traced by the red line. The persistent bubble moved ~22 μm. The bubble dynamics displayed in figures 9(a)–(l) were much clearer than those shown in figures 2(h)–(j) due to a wider scanning line interval. In the absence of persistent bubbles, only regular parallel grooves were produced, as depicted in figure 9(o).

Figure 10 details the layered fan-shaped hierarchical micro/nanostructures achieved through mobile-UPB-fs-LAL at a scanning speed of 1 mm s⁻¹ and a line interval of 10 μm, which are very similar to those shown in figure 4. The distance between the two fan-shaped layers is 18–20 μm, almost equivalent to the distance persistent bubbles move as a result of Marangoni flows. Each fan-shaped layer is composed of microgrooves with lengths of 14–24 μm. Within the same layer of fan-shaped structures, the central angles of the right (figures 10(b) and (c)), central (figures 10(e) and (f)) and left sections (figures 10(h), (i) and (k)) were 57°, 87° and 128°, respectively. On the side walls of the microgrooves, fine HSFLs with periods of 100–200 nm were discovered (figures 10(d), (g) and (j)). In the cavities of the microgrooves, sparse HSFLs were formed with gaps (figure 10(l)). In contrast to the case depicted in figure 4(c), when a deep tilted cavity was generated, the side wall was only covered by nanoprotrusions, without the formation of LIPSSs (figure 10(k)). The tilted microgrooves with microcavities confirm that the refracted pulses are no longer perpendicular to the substrates. Figures 10(m)–(o) display the structures observed at a tilt angle of 50°. As depicted, some structures were parallel to the observation direction while others were not, indicating that the bubble refractions produced a ≥50° tilt in the incident laser beam.

### 3.2.2. Circular region obtained at 0.1 mm s⁻¹

To uncover the effects of scanning speeds on surface structuring, a detailed analysis of surface structures achieved through UPB-fs-LAL
at a scanning speed of 0.1 mm s⁻¹ and a line interval of 10 μm is performed. Three large macroscopic circular regions with diameters of 300–350 μm, along with multiple macroscopic half circular regions with identical diameters, were generated by UPB-fs-LAL (figure 8(c)). Here, the topmost macroscopic circular region was chosen as representative for a detailed analysis, as depicted in figure 11(a). A low scanning speed of 0.1 mm s⁻¹ allowed more pulses to penetrate the persistent bubble. Subsequently, multiple grooves were formed (figure 11(b)), contrary to the sparsely distributed ablated spots in figure 5(a). There exists a clear structure interface (outlined by a white arc) between the structures obtained through laser ablation in gas (gas phase) and laser ablation in thin liquid layers (liquid phase), as indicated in figure 11(b). The structures that developed in the liquid phase exhibited a bright contrast, while the grooves that developed in the gas phase exhibited a dark contrast.

The layout of the structures in figure 11(b) is in line with regions 1 and 2, as defined in figures 3(d) and (e). The outermost section of the circular region in figure 11(a) was unablated due to the light blocking effect, similar to region 4, as indicated in figure 3(f). On top of the large unablated region, many arc structures were found, which corresponded to region 3, as shown in figure 3(e). Additionally, the uppermost section of the macroscopic circular structure was fully ablated, while its lower section was largely unablated, similar to the case depicted in figure 3(b). These results further confirm that when a persistent bubble initially becomes sticky, the majority of small bubbles generated by UPB-fs-LAL are absorbed by the large bubble without becoming sticky. The opposite scenario occurs in the lower section, once a bubble becomes sticky.

Figure 11(c) displays the morphologies of five ablated grooves achieved through UPB-fs-LAL, which correspond to region 2 in figure 3(b). Special attention was given to the 15–20 μm line spacing of these ablated lines, which were 50%–100% wider than the 10 μm interval set for laser scanning, and the interval of parallel grooves obtained in the absence of persistent bubbles (figure 11(a)). This can be attributed to the refraction of the incident laser light. The
The central region of the 4th groove is characterized by coarse HSFLs formed. Thus, though the pulses were modulated, UPB-fs-LAL near the center is still more likely to yield HSFLs than UHSFLs.

Figure 11(g) depicts the enlarged morphologies of the 4th and 5th grooves. The central region of the 4th groove appears bright, due to the formation of LIPSSs, as clearly displayed in figure 11(h). In order to determine the effect of the ablation environment on the formation of UHSFLs, yellow, green and red rectangles of figure 11(h), which fall within the 4th groove, were analyzed (see figures 11(i)–(k)). The central region of the 4th groove is characterized by coarse HSFLs with periods of ~130 nm (figure 11(i)), similar to the structures obtained in the gas phase shown in figure 5(f).
Figure 11. SEM images of the nanostructures obtained by UPB-fs-LAL (pulse duration: 223 fs, wavelength: 1030 nm, pulse energy: 0.5 μJ, repetition rate: 200 kHz, scanning speed: 0.1 mm s⁻¹, line interval: 10 μm). (a) SEM image of one circular area obtained by UPB-fs-LAL. (b) Green rectangle in (a). The surface morphology reveals two distinct regions, one formed by ablation in gas phase and the other formed by ablation in liquid. (c) Red rectangle in (a). Five grooves are numbered from top to bottom. The 5th groove ablated in a gas bubble is indicated by a green rectangle. (d) 1st groove and HSFLs of 1st groove (inset image). (e) 2nd, (f) 3rd, (g) 4th and 5th grooves. (h) Rectangle in (g). (i)–(k) Yellow, green and red regions in (h), respectively. (l) Comparison of the nanostructures obtained by UPB-fs-LAL in the gas phase (green rectangle in (k)) and liquid phases (rectangle in (j)). (m) Green region in (b). (n), (o) Enlarged SEM images of rectangles in (m), (n), respectively. (p) White rectangle in (a). (q), (r) Red and green rectangles in (p), respectively. (s) Arc structure produced by UPB-fs-LAL in the presence of both large/small bubbles (yellow rectangle in (a)). (t), (u) Red and green rectangles in (s), respectively. (v) Groove obtained in the absence of large persistent bubbles. (w) Hierarchical grooves decorated with HSFLs (rectangle in (v)). (x) HSFLs in (w). Scale bars in (a)–(f) are 500, 200, 40, 5 (0.5, inset image), 5 and 5 μm, respectively. Scale bars in (g)–(o) are 10, 5, 0.5, 0.5, 0.5, 0.2, 20, 2 and 0.1 μm, respectively. Scale bars in (p)–(x) are 5, 0.5, 0.5, 20, 0.5, 20, 2 and 0.5 μm, respectively. The direction of light polarization is indicated in (d).
Thus, it can be concluded that these LIPSSs were formed in the gas phase. UHSFLs with periods less than 100 nm were observed on both the upper (figure 11(j)) and lower (figure 11(k)) regions of the 4th groove. However, their morphologies were vastly different. The UHSFLs generated in the liquid phase (figure 11(j)) are characterized by long smooth ripples decorated with spherical particles, while UHSFLs generated in the gas phase are characterized by protrusions and structure rollovers (figure 11(k)). Enlarged rectangular areas of UHSFLs developed in liquid (figure 11(j)) and in gas (figure 11(k)) are compared in figure 11(l). As depicted, UHSFLs developed in gas (left figure) were more compact than those developed in liquid (right figure boxed in green). Consequently, the minimum period of UHSFLs was as small as 40 nm for UHSFLs developed in gas, which is less than 1/25th of the laser wavelength (1030 nm).

To demonstrate the reproducibility of UHSFLs generated in the gas phase, we examined the rectangular region in the ablated groove shown in figure 11(m). The region was not fully covered by debris, so coarse LIPSSs could be found (figure 11(n)). At the boundaries of these coarse LIPSSs, as illustrated in figure 11(o) (enlarged from the rectangle in figure 11(n)), UHSFLs with periods of 43 and 53 nm were found. This signifies that UHSFLs with a minimum period of ~40 nm can also be generated in gas environments close to the air–liquid-substrate interface of a large persistent bubble, as in line with the UHSFLs displayed in figures 5(i), (k), and (l). The reproducibility of UHSFLs is further examined by figures 11(p)–(r). Figure 11(p) exhibits the groove obtained by UPB-fs-LAL, which corresponds to the white rectangle shown within figure 11(a). Figures 11(q) and (r) display the nanostructure morphologies of red and green rectangles in figure 11(p), respectively. A large area of UHSFLs with periods of 41–70 nm (figure 11(q)) were found at the rim of the groove, while HSFLs with periods of 108–160 nm were found closer to the center of the groove (figure 11(r)). The fact that these UHSFLs have the same roughness as those in figure 7(d) indicates that they are formed in liquid. Therefore, we can conclude that UHSFLs with a minimum period of 40 nm can be produced in both gas bubbles and liquids.

To demonstrate the reproducibility of the bubble-size dependent generation of UHSFLs via UPB-fs-LAL at a slow scanning speed of 0.1 mm s−1, an arc structure produced in the presence of both large and small persistent bubbles was characterized, and is shown in figure 11(s) (yellow rectangle in figure 11(a)). Figures 11(t) and (u) illustrate the nanoscale morphologies of red and green rectangles, respectively. Only a few UHSFLs with periods of 76–86 nm were found at the boundary of the unablated arc area (figure 11(t)), similar to the findings in figure 7(i). Tilted HSFLs with periods of 130–160 nm were discovered within the deep groove (figure 11(u)) and had a maximum tilt angle of 28°. In previous studies, we found that tilted HSFLs can be produced on hierarchical microstructures with height gradients [10]. Here, we present another approach to obtaining tilted LIPSSs; namely, by bubble modulation of the laser light. Figure 11(v) displays an overview of the parallel grooves generated by fs-LAL in the absence of persistent bubbles. The intersections of the grooves could have resulted from the effects caused by small bubbles on the laser beam [25]. Hierarchical microgroove structures fully covered with HSFLs were achieved (figure 11(w)), as in accordance with our previous study [10]. The periods of the HSFLs were in the range of 151–203 nm (figure 11(x)). As expected, no UHSFLs were found. The microgrooves (figure 11(v)) generated in the absence of persistent bubbles were evidently much deeper than those obtained through UPB-fs-LAL (figures 11(d)–(f)), indicating that the properties of the incident laser pulses were modulated by a large persistent bubble.

3.2.3. Hierarchical micro/nanostructure. Given the possibility of a beam emitting multiple reflections inside the bubble, multi-reflected and refracted beams may be able to ablate the same region and produce novel surface structures. The varying curvatures of a spherical bubble may refract the laser beam to the same location during UPB-fs-LAL, such that successive ablation can also occur in the same region. To verify this speculation, we carefully assessed the structures in the circular area developed by stationary-UPB-fs-LAL, and found hierarchical LIPSSs in the sample obtained at a scanning speed of 0.5 mm s−1, with a line interval of 10 μm, as illustrated in figure 12(a). These hierarchical LIPSSs were composed of LSFLs and UHSFLs/HSFLs. HSFLs/UHSFLs with periods of 80–130 nm were located on the crests of LSFLs with periods of 800–900 nm (figures 12(b)–(d)). The valleys of LSFLs contained no HSFLs/UHSFLs. The orientations of LSFLs and HSFLs/UHSFLs were slightly different. The HSFLs/UHSFLs were perpendicular to the direction of laser polarization, while LSFLs were tilted by 5°, as expected. It remains unclear whether UHSFLs/HSFLs or LSFLs were formed first.

3.3. Optical properties

In optical images, the ablated Si surfaces appear black (figures 13(a) and (d)), while the unablated regions appear white. This indicates the production of black silicon. Given that black silicon often possess excellent antireflection/absorbance properties [64], the reflectance and transmittance of the ablated structures were examined. Due to the limited space within layered fan-shaped hierarchical micro/nanostructures and UHSFLs structures, reflectance in the Vis-NIR range was difficult to measure. Hence, the reflectance and transmittance of the fan-shaped hierarchical micro/nanostructures was instead evaluated in the 1.25–25 μm wavelength range. To highlight the difference in reflectance/transmittance relative to that of unablated flat Si substrates, the spectra of the flat Si substrates were set as the background signal, and the variations in reflectance/transmittance induced by UPB-fs-LAL were measured by FTIR spectroscopy.

Figures 13(g)–(i) depict the reflectance and transmittance spectra of the layered fan-shaped hierarchical micro/nanostructures achieved through mobile-UPB-fs-LAL at a scanning
speed of 1 mm s\(^{-1}\), with line intervals of 5 and 10 \(\mu m\). For simplicity, these two samples were termed N-5 and N-10, respectively. Optical images of the measurement areas of N-5 and N-10 are displayed in figures 13(a) and (d), respectively. Figures 13(b) and (e) illustrate SEM images of identical areas, while figures 13(c) and (f) exhibit magnified images of the measured surface structures. Figure 13(g) demonstrate the transmittance/reflectance percentages (%) of the ablated and unablated substrates compared to those of pristine silicon substrates via unpolarized light. Specifically, the transmittance/reflectance spectra of the flat silicon substrate were first measured and set as backgrounds, respectively, for the measurements of transmittance/reflectance of the ablated samples. As observed, both the reflectance and transmittance were significantly reduced, as compared to the unablated Si substrates. The reflectance of N-5 and N-10 increased from 5% to 33%, and from 7% to 58%, respectively, as a result of increasing the wavelength from 1.25 to 16.4 \(\mu m\). The reflectance was then gradually decreased to 1%, through increasing the wavelength to 25 \(\mu m\). The transmittance of N-5 and N-10 increased from 4.77% to 17.34% and from 8.74% to 40.27%, due to increasing the wavelength from 1.25 to 15.81 \(\mu m\). N-5 and N-10 exhibited troughs at 16.4 \(\mu m\), and was raised again to 16.19% and 38.63% at a wavelength of 17.1 \(\mu m\), and finally decreased to 0.04% and 1.20%, respectively, through increasing the wavelength to 25 \(\mu m\). The visible dip in transmittance at a wavelength of 16.4 \(\mu m\) (corresponding to a wavenumber of 609 cm\(^{-1}\)) is responsible for the two-phonon (TO + TA) mode [65], which is an intrinsic absorption band of Si [66]. Given the equation of absorbance, \(A = 1 - T - R\), it is evident that the hierarchical structures obtained by UPB-fs-LAL have a very high absorbance in the NIR-MIR range, particularly in the NIR range of 1.25–5 \(\mu m\) and the MIR range of 20–25 \(\mu m\). Xiao \textit{et al} have reported that the absorbance of microspikes, produced by fs laser ablation of Si in NF\(_3\) atmosphere, has jumped from 25% to 80% through increasing the wavelength from 2 to 16 \(\mu m\) [67].

However, the current study shows an opposite trend, which could be due to differences in surface structures. Hence, we carefully inspected for differences among the fan-shaped hierarchical structures in measured regions. Figures 13(j)–(m) reveal the hierarchical structures of samples N-5 and N-10 observed at a tilt angle of 50°. Additional layered structures were produced by UPB-fs-LAL at a line interval of 5 \(\mu m\) (figure 13(j)), double what was produced at a line interval of 10 \(\mu m\) (figure 13(l)). Furthermore, the surface roughness of the N-5 was much higher than that of the N-10, as evidenced by figures 13(k) and (m). All side walls of the N-5 fan-shaped microstructures were completely covered by HSFLs (figure 13(k)), while only a few HSFLs were discovered on the side walls of the N-10 (figure 13(m)). Since silicon gratings are good NIR and MIR absorbers [68, 69] and gratings with distinct geometries and dimensions often result in the absorption of different wavelength regions [69, 70], the higher absorbance of N-5 in the broadband can be attributed to its unique structure.
3.4. Advantages and disadvantages of UPB-fs-LAL technique

3.4.1. Advantages. Based on the results presented in the above mentioned sections, here we briefly discuss its

Considering that anisotropic structures like aperture arrays [71] possess polarization-dependent transmissive/reflective properties, the X–Y direction of the polarization-dependent reflection and transmission of hierarchical structures in the same region were evaluated using unpolarized light, as illustrated in figures 13(b) and (i), respectively. The X and Y directions were parallel and perpendicular, respectively, to the direction of the scale bar shown in figure 13(a). In both samples, the transmittance and reflectance measured in the Y direction differed from that measured in the X direction, due to structural anisotropy [72]. The N-10 sample exhibited an X-reflectance spectrum that was slightly broader than the Y-reflectance, while the reverse was observed for the transmission spectra. The N-5 sample exhibited a Y-reflectance spectrum that was much broader, but with a much lower intensity, whereas the Y-transmission spectrum in the 10–20 μm range was broader than the X–T spectrum. Similar to the trends of the unpolarized spectra (figure 13(g)), polarization-dependent transmissive (figure 13(i)) and reflective (figure 13(h)) properties were also found to be strongly dependent on structure morphology. The transmission and reflectance of the N-10 sample were much higher than those of the N-5. For instance, the maximal transmission and reflectance values in both the X and Y directions were, respectively, ∼60% and 42% for the N-10, but only 31% and 18% for the N-5.

Figure 13. Optical properties of layered fan-shaped hierarchical micro/nanostructures. (a)–(c) Optical image, corresponding SEM image and enlarged SEM image of the region measured for transmittance and reflectance, respectively, using an FTIR spectrometer. Ablation conditions were as follows. Pulse duration: 223 fs, wavelength: 1030 nm, pulse energy: 0.5 μJ, repetition rate: 200 kHz, scanning speed: 1 mm s⁻¹ and line interval: 5 μm. (d)–(f) Optical image, corresponding SEM image, and enlarged SEM image of the region measured for transmittance and reflectance using an FTIR spectrometer, respectively. Ablation conditions were as follows. Pulse duration: 223 fs, wavelength: 1030 nm, pulse energy: 0.5 μJ, repetition rate: 200 kHz, scanning speed: 1 mm s⁻¹ and line interval: 10 μm. (g) Percentages of transmittance and reflectance of hierarchical micro/nanostructures relative to that of the flat surfaces. N-5 and N-10 correspond to the line intervals of 5 and 10 μm, respectively. (h)–(i) Polarization-dependent reflectance and transmittance of as-prepared fan-shaped micro/nanostructures. Directions X and Y are parallel and perpendicular to the direction of the scale bar in (a), respectively. Enlarged SEM images of the overlapped nano LIPSSs obtained by UPB-fs-LAL at a scanning speed of 500 μm s⁻¹ and a line interval of 10 μm. (j), (k) Top-view SEM images with different magnifications. (j)–(m) SEM images with different magnifications observed at a tilt of 50°. The scale bars in (a), (b) and (d), (e), all of which have the same scale bars are 500 μm, (c)–(f) are 50 μm, (j), (l) and (k), (m) are 5 and 1 μm, respectively. The direction of light polarization is indicated in (k).
advantages compared to other laser-based techniques for constructing hierarchical micro/nanostructures.

1. If aimed to produce similar structures, time-consuming computer programming, sample tilt and focus adjustment for accurately controlled ablation have to be all taken into account. Persistent bubbles offer an ideal effort-efficient medium for beam tilt to realize self-programming of fan-shaped hierarchical micro/nanostructures. In absence of persistent bubbles, only grooved micro/nanostructures [7, 10] can be produced on Si by fs-LAL.

2. Spatial light modulator has been used to generate different kinds of polygonal beams [73] for hierarchical micro/nanostructuring, compared with which UPB-fs-LAL is a cost-efficient method for constructing arrayed patterns without the need of any optics.

3. The discovery of large areas of UHSFLs shown in figure 7(b) indicates that the persistent bubbles are able to modulate the beam into a state that facilitates the generation of LIPSSs with smaller periods, well beyond the ability of unmodulated Gaussian beam for nanostructuring.

### 3.4.2. Disadvantages

The disadvantages of this technique are also obvious.

1. The bubble dynamics is hard to control, including location, size, mobility and collapse of persistent bubbles.
2. The beam reflection, refraction and scattering induced by persistent bubbles are very complex, which make it difficult to manipulate the properties of beams so that unpredicted random ablation is normally triggered.

### 4. Conclusion

This paper presents a state-of-the-art UPB-fs-LAL technique that enables the formation of novel tailed concentric-circle macrostructures. Depending on the state of the bubbles, UPB-fs-LAL can be further classified into stationary- and mobile-UPB-fs-LAL, which yield tailed and concentric-circle macrostructures, respectively. Tailed macrostructures consist of layered fan-shaped hierarchical micro/nanostructures with central angles of 45°–141°. They are generated by tilted fan-shaped beams, which are beam refracted by persistent bubbles. The refraction of large persistent bubbles causes a ≥50° tilt in the incident laser beam, while different curvatures from various sections of a persistent bubble induce fan-shape scanning during line-by-line scanning. Marangoni flow drives the movement of the bubbles so that continuous fan-shape scanning would be activated during a bubble’s movements. The layer spacing of fan-shaped structures can be adjusted by altering the scanning line interval, while the lengths of the tilted macrostructures can be controlled by shifting the scanning speed. High scanning speeds (e.g. 1 mm s\(^{-1}\)) yield long tailed macrostructures, while slow scanning speeds (e.g. 0.1 mm s\(^{-1}\)) prevent the movement of persistent bubbles. This is because rapid scanning enables the contact line to bend extensively downwards, while gradual scanning only allows spot bending of the contact line. In the latter case, it becomes difficult to push the bubble steadily downward. At a fixed scanning rate, smaller scanning intervals enable the formation of denser fan-shaped microstructures, decorated with much finer HSFLs with periods of 100–200 nm, which signify significantly lower reflectance and transmittance in the NIR-MIR range.

LSFLs, HSFLs, and UHSFLs with periods of 550–900, 100–200, and 40–100 nm, respectively, are simultaneously produced near the center of persistent bubbles, due to the complex attenuation of laser properties by large persistent bubbles. Successive ablation, occurring in the same region via laser beams refracted and reflected by the bubble, allows the formation of hierarchical nanostructures that contain HSFL/ UHSFL-decorated LSFLs. The overlapped LIPSSs presented in this study may inspire greater devotion to constructing hierarchical nanostructures through laser ablation, rather than conventional lithography for complex nanostructuring. In concentric-circle macrostructures, large areas of UHSFLs with periods as small as 40 nm are discovered. Forty nanometers are the smallest period to ever be obtained for a Si-HSFL. Breaking the bottleneck for the formation of UHSFLs for most commercial fs lasers at repetition rates of kHz offers opportunities for black silicon preparation with higher surface areas. Considering its ability to form UHSFL on Si surfaces, this technique can also be employed to develop UHSFLs on other materials, including metals, which will be further explored in the future. Therefore, the UHSFLs presented in this study can potentially also be applied to surface-enhanced Raman scattering (SERS) detection [61] during which the periods of LIPSSs greatly influence enhancement of the Raman signal [74]. We hope that the insights gained into the formation mechanism of bubble-assisted fs-LAL will also inspire further research on how to improve control over the uniformity and sizes of LIPSSs and study the correlation of surface morphology with particle productivity [75].

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