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Irregular LIPSS produced on metals by single linearly polarized femtosecond laser

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Abstract
Currently, supra-wavelength periodic surface structures (SWPSS) are only achievable on silica dielectrics and silicon by femtosecond (fs) laser ablation, while triangular and rhombic laser induced periodic surface structures (LIPSS) are achievable by circularly polarized or linear cross-polarized femtosecond laser. This is the first work to demonstrate the possibility of generating SWPSS on Sn and triangular and rhombic LIPSS on W, Mo, Ta, and Nb using a single linearly polarized femtosecond laser. We discovered, for the first time, SWPSS patches with each possessing its own orientation, which are completely independent of the light polarization direction, thus, breaking the traditional rules. Increasing the laser power enlarges SWPSS periods from 4–6\ \mu m to 15–25\ \mu m. We report a maximal period of 25\ \mu m, which is the largest period ever reported for SWPSS, \sim 10 and \sim 4 times the maximal periods (2.4\ \mu m/6.5\ \mu m) of SWPSS ever achieved by fs and ns laser ablation, respectively. The formation of triangular and rhombic LIPSS does not depend on the laser (power) or processing (scan interval and scan methodology) parameters but strongly depends on the material composition and is unachievable on other metals, such as Sn, Al, Ti, Zn, and Zr. This paper proposes and discusses possible mechanisms for molten droplet generation/spread/solidification, Marangoni convection flow for SWPSS formation, and linear-to-circular polarization transition for triangular and rhombic LIPSS formation. Reflectance and iridescence of as-prepared SWPSS and LIPSS are characterized. It was found that besides insufficient ablation on W, the iridescence density of Ta-, Mo-, Nb-LIPSS follows the sequence of melting temperatures: Ta > Mo > Nb, which indicates that the melting temperature of metals may affect the regularity of LIPSS. This work may inspire significant interest in further enriching the diversity of LIPSS and SWPSS.

Keywords: LIPSS, SWPSS, femtosecond laser, antireflectance, triangular LIPSS, iridescence, rhombic LIPSS

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1. Introduction

Laser induced periodic surface structuring (LIPSS) was discovered in 1965 [1]. The following decades witnessed rapid advancements in producing LIPSS on different metals, polymers, semiconductors, and glasses and their applications in various fields [2–7]. LIPSS structures possessing either a colorful iridescence [7] or a black color [8] are excellent biomimetic interfaces [6]. The convenience of producing LIPSS on different materials has made the direct laser writing technique more attractive than traditional expensive lithography techniques for nanostructuring. According to the decreased ratio of the LIPSS period to the laser wavelength, LIPSS can be divided into supra-wavelength periodic surface structures (SWPSS) and low/high/ultrahigh spatial frequency LIPSS (LSFL/HSFL/UHSFL). The SWPSS, whose period is normally larger than the laser wavelength, is generally prepared by nanosecond (ns) lasers because of their distinct thermal effects, but seldom by femtosecond (fs) lasers. Table 1 displays the reported scanning electron microscope (SEM) morphologies of SWPSS and summarizes the preparation conditions and the SWPSS periods. SWPSS is merely achievable on silica dielectrics [9–12] and silicon [13, 14] by fs laser ablation in air (FLAA). Although SWPSS with periods in the range of 3–6.5 µm has been produced on chromium (Cr) and gold (Au) films using nanosecond lasers [15–17], no report has developed SWPSS on a metal target via fs laser ablation. All SWPSS were produced by static multi-pulse fs ablation. So far, the maximal period of SWPSS obtained by fs laser ablation is 2.4 µm [14]. One may wonder how SWPSS will evolve if a large-scale area of SWPSS is scanned and whether the periods of SWPSS can be further enlarged, and to which extent the period of SWPSS can be reached. The formation of SWPSS is associated with Marangoni convection hydrodynamics such as convection roll-driven hydrodynamic phenomena [10] and Marangoni convection properties such as capillarity convection force [15]. It is still questionable whether some other factor that can govern the SWPSS states has not yet been discovered and reported. This work seeks answers to these questions on the basis of fs laser of SWPSS on tin (Sn) metal targets.

Many efforts have also been devoted to manipulating the properties (orientation, period and morphology) of LIPSS and enriching LIPSS’s diversity by changing the atmospheres [8, 18], modulating light properties [19–21], and introducing external stimuli such as bubbles [22] and shockwaves [23]. Among all novel LIPSS structures, triangular and rhombic LIPSS are one of the most interesting series because of their high homogeneity and the possibility for large-scale production. Triangular and rhombic LIPSS have been produced on tungsten (W) [24, 25], chromium (Cr) [26], cobalt (Co) [27], nickel (Ni) [7], stainless steel [28–31], and metal alloy [32] by a single beam with a circular/azimuthal/radial polarization or two time-delayed fs laser beams with cross linear polarizations, as summarized in table 2. Triangular and rhombic LIPSS may be formed via the non-linear convection flow mechanism [31] or self-organization driven by Coulomb repulsion [27] or noncollinear excitation of two surface plasmons [26]. No report has proven the feasibility to produce triangular and rhombic LIPSS using a single linearly polarized laser.

This work breaks the empirical laws for the preparation of both SWPSS and triangular/rhombic LIPSS and, for the first time, demonstrates the possibility of developing SWPSS on Sn and triangular and rhombic LIPSS on Ta, Mo, and Nb via single linearly polarized FLAA. The surface structures obtained by FLAA were characterized by SEM, which can be used for a direct comparison with the counterparts presented in tables 1 and 2. The possible mechanisms for the yield of SWPSS and triangular and rhombic LIPSS on different metals are discussed.

2. Experimental

A femtosecond laser (pulse duration of 400 fs, wavelength of 1030 nm, and repetition rate of 400 kHz) was used for the FLAA of Sn, Ta, Mo, Nb, W, Ti, Al, Zn, and Zr, as schematically illustrated in figure 1(a). The samples were scanned at a scan speed of 200 mm s−1 by a high-speed galvano-mirror scanner along different scan directions, as illustrated in figure 1(b). Special structures (figures 1(c) and (d)) were only discovered on Sn, W, Ta, Mo, and Nb, while normal LIPSS was produced on the Ti, Al, Zn, and Zr surfaces. The scan line intervals were set at 5, 10, 15 and 20 µm. Single scan and double scan were both performed for FLAA of Mo to demonstrate the repeatability of triangular and rhombic LIPSS. Different laser powers of 15, 8, 5, and 2 W were used for FLAA. The surface morphologies were characterized by SEM (NOVA NanoSEM 230, FEI). The reflectance of the samples in UV-to-NIR and NIR-to-MIR ranges was analyzed by UV–Vis (Lamda 950, PerkinElmer, Inc.) and FTIR spectroscopy (Nicolet 6700, Thermo Fisher). To simplify the description of the samples obtained under different conditions, the samples are named by material-power-interval. For example, Sn-2W-15 µm refers to a sample that was prepared by FLAA of Sn at a laser power of 2 W, and scan interval of 15 µm. The scan speed was constant at 200 mm s−1 for all samples. For iridescent observation, an LED white light at the power of 1 W was used for illumination well above the sample. A cell phone camera (Hua wei mate 20) was used to capture the optical images of ablated surfaces.

3. Results and discussion

3.1. SWPSS on Sn

Figure 2 displays the SEM and confocal microscopy morphologies of the structures obtained by FLAA of Sn at laser powers of 2, 5, and 8 W and a scan interval of 15 µm. The periods of SWPSS obtained at 2 W ranged from 4 to 6 µm (figure 2(a)), about 4–6 times the laser wavelength (1.03 µm), much larger than the periods of already published SWPSS prepared by fs lasers (table 1). The depth of such SWPSS is ~10 µm (figure 2(d)). Increasing the laser power to 5 W for FLAA
Table 1. Summary of SWPSS prepared by fs laser ablation. All figures are adapted with permission of publishers. Reprinted figure with permission from [10]. Copyright (2016) by the American Physical Society. Reprinted with permission from [9] © The Optical Society. Reproduced from [11], CC BY 4.0. Reprinted from [13]. Copyright (2020), with permission from Elsevier. Reprinted with permission from [14]. Copyright (2018), AIP Publishing LLC. Reproduced from [12]. CC BY 4.0.

| SEM morphology | Environment                  | Laser parameters | Materials            | Period    | References |
|----------------|-----------------------------|------------------|----------------------|-----------|------------|
| Gaussian beam, air, room temperature | 170 fs, 513 nm, 3.33 cm⁻², NP = 30 | SiO₂ | 0.6–1 µm | [10] |
| Air, room temperature | 260 fs, 800 nm, 10 Hz, 4.9 J cm⁻², NP = 30 | K9 glass (SiO₂) | 1.3 µm | [9] |
| Air, 1200 °C | 300 fs, 1025 nm, 1 kHz, 4.86 J cm⁻², N = 5 | Fused silica | 1.1 µm | [11] |
| Air, room temperature | 180 fs, 1026 nm, 1 kHz, 0.4 J cm⁻², N = 200 | Si | 2 µm | [13] |
| Air, room temperature | 100 fs, 800 nm, 10 Hz, 30 µJ, N = 50 | Si | 1.9–2.4 µm | [14] |
| Air, room temperature | 230 fs, 1030 nm, 50 kHz | Fused silica | 930–980 nm | [12] |
| Patched SWPSS with different orientations | 400 fs, 1030 nm, 400 kHz | Sn | 4–25 µm | This work |

led to the enlargement of SWPSS’s periods to the range of 15–25 µm (figure 2(b)) and increased the SWPSS’s depth to ~20 µm (figure 2(d)). Currently, the largest SWPSS period is 25 µm, ~10 and ~4 times the maximal period (2.4 µm [14] / 6.5 µm [17]) of SWPSS ever achieved by fs and ns laser ablation, respectively. It was reported that a higher substrate temperature facilitates the formation of SWPSS and can trigger the evolution of LSFLs into SWPSS on silica when the substrate temperature exceeds 850 °C [11], which may explain the increase in the SWPSS period. However, when the laser power increased to 8 W, many regions were covered by smooth wavy patches (figures 2(e) and (f)), which are deemed to originate from the solidification of strong molten layers. Figure 2 indicates that increasing the laser power significantly enhances the thermal effect because of the low melting temperature (232 °C) of Sn, which creates a favorable environment for the formation of larger and wider SWPSS. But the thermal effect should be controlled in a certain range; otherwise, the surface structures will be covered by the molten layers (figure 2(e)).

Of great interest, SWPSS with different orientations were produced (figures 2(a)–(d) and 3(a)–(f)) completely independent of the linear light polarization direction, which is considered the most crucial factor to govern the LIPSS’s direction [2]. This discovery further enriches the diversity of SWPSS ever reported, including quasi-periodical SWPSS [15] and transverse and inclined SWPSS [17]. The formation of unusual SWPSS indicates the emergence of a new mechanism that differs from the conventional mechanisms, including interference, surface plasmon polaritons (SPPs), and second
Table 2. Summary of triangular and rhombic LIPSS reported so far and the preparation conditions.

| Beam properties       | Laser parameters                      | Materials         | Period        | References |
|-----------------------|---------------------------------------|-------------------|--------------|------------|
| Tri-LIPSS Circular    | 1030 nm, 7 ps, 400 kHz                | CoCrMo            | 0.83 λ       | [32]       |
| Tri-LIPSS Circular    | 1032 nm, 310 fs, 0.25–2 MHz           | Stainless steel (X6Cr17) | 0.90 λ       | [28]       |
| Tri-LIPSS Circular    | 1032 nm, 310 fs, 500 kHz              | Stainless steel (X6Cr17) | 0.81–0.95 λ  | [29]       |
| Tri-LIPSS Circular    | 1030 nm, 200 fs, 200 kHz              | Stainless steel   | 0.87 λ       | [30]       |
| Tri-LIPSS Linear and  | 1030 nm, 350 fs, 100 kHz              | Stainless steel   | 0.89 λ       | [31]       |
| Tri-LIPSS Linear      | 800 nm, 50 fs, 1 kHz                  | W                 | 0.89 λ       | [25]       |
| Tri-LIPSS Linear      | 800 nm, 50 fs, 1 kHz                  | W                 | 0.76 λ       | [24]       |
| Tri-LIPSS Linear      | 800 nm, 40 fs, 1 kHz                  | Cr                | 0.85 λ       | [26]       |
| Tri- and rhombic-LIPSS| 800 nm, 35 fs, 1 kHz                  | Co                | 0.81–0.925 λ | [27]       |
| Rhombic LIPSS         | 170 fs, 1 kHz, 1026 nm, Ni            | Ni                | 0.76 λ       | [7]        |
| Tri- and rhombic LIPSS| 1030 nm, 400 fs, 400 kHz              | Mo, Ta, Nb        | 0.74 λ       | This work  |

λ—wavelength, ps—picosecond, fs—femtosecond, Tri-LIPSS—triangular LIPSS.

harmonic generation [2, 18]. Since these irregular SWPSS are very similar to the convection patterns triggered by temperature gradients [33], it is proposed that Marangoni convection flows propagating at speeds of 60–80 m s⁻¹ [15, 34, 35] are responsible for the formation of patched SWPSS in different orientations. The tadpole-like protrusions marked by the dashed circles in figures 3(g)–(i) are good indicators of the occurrence of Marangoni convection flows [10] and give hints to the flow directions of molten layers. SWPSS structures (figures 3(b)–(f)) at the boundaries of patches (figure 3(a), marked by yellow lines) are very complex. A distinct wall structure formed in the foremost part along the SWPSS’s flow direction (figures 3(b) and (d)), where some SWPSS squeezed into bimodal SWPSS. The flow direction of SWPSS can simultaneously bifurcate upward and downward (figure 3(e)), so bifurcated SWPSS were created. A >90° sudden alteration of the flow directions was also found (figures 3(e) and (f)), leading to the formation of porous SWPSS and short SWPSS. Minor variations in the flow direction yielded broken-line-shaped SWPSS (figure 3(c)).

Figure 4 displays the possible formation mechanism of SWPSS during the FLAA of Sn at laser powers of 2, 5, and 8 W. The melting states and sizes of molten droplets depend on the laser powers. Higher laser powers generate larger molten droplets and induce higher melting rates. Previous reports have shown the sequential, layer-by-layer assembly of molten Sn droplets for three-dimensional manufacturing [36]. So, it is reasonable to deduce that at a laser power of 2 W, the interaction of fs laser and the Sn target will generate many separated molten droplets. High temperatures of molten droplets verify that remelting the substrate produces a robust bond between the spreading molten droplets and the ablated substrate [36]. The spread of molten droplets leads to the formation of SWPSS patches. Each molten droplet has a unique temperature gradient which drives the movement of the Marangoni convection flow from the hot region to the cold region [33]. Meanwhile, the convection forces, including the thermo-capillarity (Marangoni) shear stress and the stress originating from variations in the radius of the curvature.

Figure 1. (a) Schematic illustration of FLAA. (b) Line-by-line scan method and three scan methodologies used for FLAA. (c) and (d) Schematic of SWPSS and triangular and rhombic LIPSS prepared by FLAA.
of molten droplets, govern the orientations of SWPSS [15]. Due to the gentle thermal effect (2 W-FLAA), Marangoni convection flows, which are the precursors of SWPSS, tend to solidify very fast, so SWPSS patches with different orientations formed. The formation of microscale holes among the SWPSS arrays (figure 3) may be attributed to the gas capsulation [37] because the existence of ripple structures on molten Sn droplets can increase the possibility of gas capsulation [38] or complex fluidity of Marangoni flow such as Marangoni bursting [39] which has been proven to take place during laser ablation of metals [8].

When a stronger thermal effect was triggered at 5 W-FLAA, no patched SWPSS were generated due to the formation of larger droplets, which can promote the connection/coalescence of molten droplets with each other during their ejection/spread/cooling processes. In addition, higher power must have increased the ablation productivity, so the density of molten droplets should have increased. The molten droplets may be concurrently and sequentially coalesced, analogous to the gradual increase in the volume of persistent bubbles generated during line-by-line fs laser ablation in water [22]. Further increasing the laser power to 8 W enhanced the thermal effect, which generated larger molten droplets with a longer lifetime. They will flow/eject on existing SWPSS, leading to the formation of smooth islands among SWPSS (figures 2(c), (d) and 4). Previously, only microporous structures featured by a density of nanodroplets and cavities have been produced on Sn via fs laser ablation in ethanol [40]. Besides enriching the SWPSS diversity, this work also diversifies the variety of Sn surface structures, which have the potential to be applied for wettability control [41, 42] and underwater bubble manipulation [43–45].

3.2. Triangular and rhombic LIPSS on W, Mo, Ta and Nb

Eight other kinds of metals, including Al, Zn, Ti, Zr, W, Mo, Ta, and Nb were ablated by FLAA at the laser power of 2 W to check the structure difference. Normal LIPSS
and indiscernible LIPSS were produced on Al/Zr/W/Mo (figures 5(a), (d)–(f)), and Zn/Ti (figures 5(b) and (c)), respectively. LIPSS on ablated Al and Zr surface is densely decorated by particles, while LIPSS on the Zn surface features a large number of pores. On the W/Mo surfaces, besides normal parallel LIPSS, spasmodic triangular and rhombic LIPSS were found in the rectangular regions marked in figures 5(e) and (f). A dense array of triangular and rhombic LIPSS was produced on Ta (figure 5(g)) and Nb (figure 5(h)), which formed among traditionally longitudinal LIPSS. The period of normal LIPSS was ∼650 nm, while the period of triangular LIPSS was ∼760 nm. High spatial frequency LIPSSs were generated on a Ti surface with a period of ∼380 nm (figure 5(c)). UHSFLs [8] with periods of tens of nm are located in the trenches of LIPSS on the ablated Nb sample (figure 5(i)). Because surface melting and resultant Marangoni bursting has been proven to be necessary for the formation of LIPSS [46] and UHSFLs [8].

It was deduced that gentle or cold melting occurs to ablated metals during FLAA even though the melting temperature of Mo, Ta, and Nb are as high as 2620 °C, 3017 °C, and 2477 °C, respectively.

We wondered whether the formation of triangular and rhombic LIPSS strongly depends on the laser and processing parameters. Choosing the Mo substrate as a representative, FLAA was performed with a laser power of 5 W, scan intervals of 5, 10, 15, and 20 µm, and two scan methodologies (single-scan and double-scan). Figures 6(a)–(c) show that triangular LIPSS formed among normal LIPSS (figure 6(b)) for the Mo-5 W-5 µm sample. Increasing the scan intervals to 10, 15, and 20 µm also enabled the formation of rhombic LIPSS (figures 6(d) and (f)) and triangular LIPSS (figure 6(e)). Same-direction double-scan (figures 6(g)–(i)) and cross-direction double-scan (figures 6(j)–(l)) are also capable of creating triangular and rhombic LIPSS among normal LIPSS.

Unlike uniform triangular and rhombic LIPSS prepared by circularly polarized laser and linear cross-polarized beams [27, 31], the layouts of triangular and rhombic LIPSS are heterogeneous (figures 6(j)–(l)), indicating that the influential factor is confined to local regions and may vary dramatically in different regions. Compared to the cross-polarized beams, which only allow a processing parameter window to yield triangular and rhombic LIPSS [27], this work shows that their formation is independent of laser power, scan line interval, and scan methodology while adopting a single linearly polarized fs laser. But the homogeneity and the area of triangular and rhombic regions are not comparable.

Many mechanisms have been proposed for the formation of triangular and rhombic LIPSS. One is the non-linear convection flow [31] triggered by strong temperature gradients. Another example is the hexagonal convection flow matrix [33]. If this mechanism occurs, the active convection flows should be subjected to the irradiation of tens of pulses. As a consequence, the flow structure should be very complex like Sn-SWPSS (figures 2(a)–(d)) rather than leading to the formation of homogeneous LIPSS with sharp edges. Hence, the non-linear convection flow mechanism can be ruled out for the formation of triangular and rhombic LIPSS.
obtain during FLAA [51].

ted that ZnO particles produced by laser ablation in water start subjected to a high oxidation rate and nucleation/growth of metal oxide crystals. That is why porous LIPSS rather than contrast, metals with lower temperatures may become melted of LIPSS, such as linear-to-circular polarization transition. In FLAA, so it is possible to trigger the 'metasurfaces' functions temperatures are resistant to high temperature increases during metals with high melting-temperatures are resistant to high temperature increases during LIPSS, so it is possible to trigger the 'metasurfaces' functions of LIPSS, such as linear-to-circular polarization transition. In contrast, metals with lower temperatures may become melted and restructured by the following incident pulses or may be subjected to a high oxidation rate and nucleation/growth of metal oxide crystals. That is why porous LIPSS rather than smooth LIPSS is attained on Zn surface. Ishikawa et al reported that ZnO particles produced by laser ablation in water start growing at the temperature of 60 °C [50], which is easy to obtain during FLAA [51].

LIPSS obtained by FLAA of metals are normally composed of both pure metals and metal oxides [48] with the latter being the dielectric component. Although metal and dielectric components are not layer-by-layer constructed like metasurfaces [52], it is speculated that they should function similarly to metasurfaces (figure 7). One function of metasurfaces is linear-to-circular polarization transition, which is realizable using dielectric gratings with periodic metallic strips [53] or metallic zigzag arrays [54], analogous to LIPSS structures presented in this work. Hence, it is deduced that existing LIPSS may act as a linear-to-circular polarizer to trigger the formation of triangular and rhombic LIPSS upon successive laser irradiation. Triangular LIPSS can only be produced by adopting optimized laser fluences and scanning speeds [29]. Unoptimized conditions produce a mixture of normal LIPSS and triangular LIPSS [29]. In our experiments, laser power and scanning speed were unoptimized. The scanning speed and repetition rate were set at 200 mm s⁻¹ and 400 kHz, respectively, which means there were two pulses in every micron distance and a very high overlap ratio of pulses. Since each laser pulse can induce the formation of LIPSS [55], it is highly likely that the existing LIPSS structures interact with the incoming light to change the optical field properties and result in the alteration of LIPSS’s layout. Anisotropic LIPSS structures have already been used to tune light polarization by altering the scattering of orthogonal and parallel polarized light [56]. Hence, the modulation of the linearly polarized light into an azimuthally/circularly polarized light by LIPSS takes place. No matter whether single scan or double scan methodologies are adopted, the mixture of parallel and triangular LIPSS are achievable, as shown in figure 6. If the linear-to-circular transition really takes places, the chance of this happening should be rare and confined to a local region, which can be deduced from very limited areas of triangular and rhombic LIPSS and the randomness of their layouts. Another formation mechanism that may induce the formation of triangular and rhombic LIPSS is the interference of surface plasmon waves with incident light, which is capable of producing crosshatch structures upon laser irradiation of square or triangle Au metal structures [57]. This work and another work published by Jia et al [47] explore the formation of split structures via SPP enhancement. The ejected or deposited particles irradiated by laser pulses is another factor that can induce the formation of bent LIPSS [58] by enhancing the electric field [59]. However, this factor can only induce random bending of LIPSS, but it cannot induce the triangular LIPSS shown in figure 6(g). Other than split and bent LIPSS, nanocavities and nanotrenches on the ablated Ti surface indicate the complexity during FLAA of Ti, which may be associated with the third harmonic generation [60].

### Table 3. Melting temperatures of different transition metals.

| W | Ta | Mo | Nb | Zr | Ti | Al | Zn |
|---|----|----|----|----|----|----|----|
| T (°C) | 3422 | 3017 | 2620 | 2477 | 1852 | 1725 | 660 | 419 |

Figure 6(h) displays the possibility to generate split LIPSS, which has also been discovered on stainless steels treated by fs laser ablation [47]. It is deemed that the localization of the incident laser light in the protuberances of LIPSS leads to the formation of split LIPSS [47]. Hence, the triggering of extra electric fields or SPPs upon the interaction of the incident light and the existing LIPSS should take place. Hence, besides the SPPs responsible for the formation of LIPSS, two other local SPPs in the other two directions should also be generated [26], which promote the formation of triangular and rhombic LIPSS.

Table 3 lists the melting temperatures of the transition metals used for our experiments. It is clear that triangular and rhombic LIPSS mainly formed on the Ta/Mo/Nb transition metals with melting temperatures between 2000 °C and 3000 °C. Triangular and rhombic LIPSS were seldom found on the W sample. In our previous report, we performed FLAA on W with different scan intervals at a laser power of 5 W [48]. Only split LIPSS was produced (similar to figures 6(g) and (h)) because of a strong coupling of the incident laser and the surface plasmons in high-density plasma states [47]. Laser ablation of metals normally induces a significant increase in the surface temperature [49]. Metals with high melting-temperatures are resistant to high temperature increases during FLAA, so it is possible to trigger the ‘metasurfaces’ functions of LIPSS, such as linear-to-circular polarization transition. Local SPPs in the other two directions should also be generated. Hence, besides the SPPs responsible for the formation of LIPSS, two other local SPPs in the other two directions should also be generated [26], which promote the formation of triangular and rhombic LIPSS.

Figure 7. Possible formation mechanism of the split LIPSS and triangular and rhombic LIPSS upon laser irradiation of existing LIPSS. Red colored region indicates the pulse irradiation region. M/MOₓ—metal and metal oxide, used for a qualitative demonstration.
3.3. Antireflectance and iridescence of SWPSS and LIPSS

Figure 8(a) displays the reflectance of an unablated Sn sample and Sn-SWPSS samples produced by FLAA at laser powers of 2, 5, and 8 W. It is clear that laser ablation can significantly reduce reflectance, so the ablated surfaces are good candidates for antireflective applications [8, 24, 61]. The antireflective performances of ablated surfaces depend on the structure’s properties. Larger and wider Sn-5 W-SWPSS (blue line in figure 8(a)) are more antireflective than smaller and shallower Sn-2 W-SWPSS (red line in figure 8(a)), which is due to the higher trapping ability for UV-to-NIR broadband light by deeper SWPSS trenches. This deduction is confirmed by the superior antireflectance performance of Sn-8 W-SWPSS (green line in figure 8(a)) than that of Sn-2 W-SWPSS even though Sn-8 W-SWPSS is covered by molten layers (figures 2(e) and (f)). Figure 8(b) shows the reflectance of all nine samples prepared by FLAA at a laser power of 2 W.

power of 2 W. Even though the emergence of triangular and rhombic LIPSS can increase the surface areas of Mo-, Ta-, and Nb-LIPSS, their antireflectance performances are not the best. The best UV-to-NIR ultrabroad antireflective surface is Ti-, while the best visible-range antireflective surface is Zr-LIPSS, which may be due to the formation of ZrOx in light of reflectance similarity [62]. Except the Zn sample, which has a distinct reflectance valley in the NIR range, the reflectance of most LIPSS/SWPSS surfaces increases as the wavelength increases. Hence, it can be concluded that the antireflective performance is a synergistic effect combing both surface composition and surface structure. The analysis of the effect of surface composition on antireflectance is beyond the scope of this manuscript, which will be done in another work.

LIPSS is a kind of refraction grating that enables the observation of various iridescence under different observation angles [7, 41, 63], so they are good candidates to be directly used as biomimetic colorful surfaces [6] or in anticounterfeiting applications [64–66]. In this regard, we characterize the iridescence of as-prepared structured surfaces under the illumination of white light, as shown in figure 8(c). The optical images of Sn, Zr, Zn, Ti, W, Al, Nb, Mo, and Ta samples taken at the capture angle of 45° and illumination angles of 0°, 15°, and 30° are shown in figures 8(d)–(l). Sn-SWPSS does not have iridescence because of multi-orientations and the existence of enormous pores, which can efficiently trap light rather than diffract light. Furthermore, Zr, Zn, and Ti samples do not possess iridescence (figures 8(e)–(h)) due to their high roughness and structural irregularity (figures 5(b)–(d)). Reducing the roughness of Al-LIPSS (figure 5(a)) revealed a weak iridescence (figure 8(i)). The weak iridescence of W-LIPSS is due to the irregularity of LIPSS and the existence of smooth regions (figure 9(a)). The formation of smooth regions originates from

Figure 8. (a) and (b) Antireflectance of the Sn-SWPSS and all nine metal SWPSS/LIPSS in the UV–Vis–NIR range. (c) Experimental setup for the iridescence measurement with white light illumination at angles of 0°, 15°, and 30°. (d)–(l) Optical images of Sn, Zr, Zn, Ti, W, Al, Nb, Mo, and Ta samples taken at the capture angle of 45°, respectively. LIPSS orientation is horizontal, as marked by the orange arrow. All samples are obtained by FLAA at a laser power of 2 W.

Figure 9. (a)–(d) SEM images of LIPSS structures obtained by FLAA of W, Nb, Mo, and Ta at a laser power of 2 W.
insufficient ablation. That is, very high melting temperatures of W only enables a partial melting during FLAA at a laser power of 2 W. Our previous report demonstrated the possibility of inducing complete ablation via FLAA at 5 W to achieved a good iridescence on W [48]. Interestingly, the iridescence of Nb, Mo, and Ta follows the sequence of melting temperatures shown in table 3. Since iridescence is greatly dependent on the regularity and uniformity of LIPSS [67], it is reasonable to deduce that the regularity of LIPSS follows the sequence of Ta > Mo > Nb, which is confirmed by their structure morphologies (figures 9(b)–(d)). LIPSS has been verified to be strongly dependent on the surface melting [18, 46], so the melting temperature of the ablated materials should be a critical factor that determines the states of LIPSS.

4. Conclusion

In summary, this work demonstrated the creation of unique SWPSS on Sn and produced triangular and rhombic LIPSS on W, Mo, Ta, and Nb by FLAA. Increasing the laser power from 2 W to 5 W significantly increased the periods of SWPSS from 4–6 µm to 15–25 µm, thus, allowing us to achieve the largest SWPSS ever reported. The generation of different sizes of molten Sn droplets and their coalescence/spread/solidification together with Marangoni convection flows are considered to be the driving force behind the formation of SWPSS patches with each patch having its own SWPSS orientation. Further increasing the laser power produced an ultrastrong thermal effect with a longer lifetime of molten layers, which will solidify on the SWPSS. The formation of triangular and rhombic LIPSS is dependent on the material property, independent of the processing parameters. Our analysis of multiple LIPSS’s iridescences, surface morphologies, and metal melting temperatures, suggests that transition metals with melting temperatures higher than 2000 °C are excellent substrates to be endowed with triangular and rhombic LIPSS, which form via linear-to-circular polarization transition mechanism upon the impact of a single linearly polarized fs laser. The SWPSS and LIPSS containing certain percentages of triangular and rhombic LIPSS are good candidates for antireflective applications. Mo and Ta LIPSS surfaces possess good iridescence with the potential to be used for anti-counterfeiting applications.

Conflict of interest

The authors declare no competing financial interests.

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References

[1] Birnbaum M 1965 Semiconductor surface damage produced by ruby lasers J. Appl. Phys. 36 3688–9
[2] Bonse J, Höhn S, Kirner S V, Rosenfeld A and Krüger J 2017 Laser-induced periodic surface structures—a scientific evergreen IEEE J. Sel. Top. Quantum Electron. 23 9000615
[3] Bonse J 2020 Quo vadis LIPSS?—recent and future trends on laser-induced periodic surface structures Nanomaterials 10 1950
[4] Bonse J and Gräf S 2020 Maxwell meets Marangoni—a review of theories on laser-induced periodic surface structures Laser Photonics Rev. 14 2000215
[5] Zhang B, Liu X F and Qiu J R 2019 Single femtosecond laser beam induced nanogratings in transparent media-mechanisms and applications J. Materiomics 5 1–14
[6] Stratakos E et al 2020 Laser engineering of biomimetic surfaces Mater. Sci. Eng. R Reports. 141 100562
[7] Skoulas E, Manousaki A, Potakis C and Stratakos E 2017 Biomimetic surface structuring using cylindrical vector femtosecond laser beams Sci. Rep. 7 45114
[8] Zhang D S, Ranjan B, Tanaka T and Sugioka K 2020 Carbonized hybrid micro/nanstructured metasurfaces produced by femtosecond laser ablation in organic solvents for biomimetic antireflective surfaces ACS Appl. Nano Mater. 3 1855–71
[9] Xu S-Z, Sun K, Yao C-Z, Liu H, Miao X-X, Jiang Y-L, Wang H-J, Jiang X-D, Yuan X-D and Xu Z-T 2019 Periodic surface structures on dielectrics upon femtosecond laser pulses irradiation Opt. Express 27 8983–93
[10] Tsibidis G D, Skoulas E, Papadopoulos A and Stratakos E 2016 Convection roll-driven generation of supra-wavelength periodic surface structures on dielectrics upon irradiation with femtosecond pulsed lasers Phys. Rev. B 94 081305
[11] Gräf S, Kunz C, Engel S, Derrien T J Y and Müller F A 2018 Femtosecond laser-induced periodic surface structures on fused silica: the impact of the initial substrate temperature Materials 11 1340
[12] Schwarz S, Rung S, Esen C and Hellmann R 2018 Surface plasmon polariton triggered generation of 1d-low spatial frequency LIPSS on fused silica Appl. Sci. 8 1624
[13] Allahyari E, Nivas J J, Skoulas E, Bruzzese R, Tsibidis G D, Stratakos E and Amoruso S 2020 On the formation and features of the supra-wavelength grooves generated during femtosecond laser surface structuring of silicon Appl. Surf. Sci. 528 146607
[14] Nivas J J, Anoop K K, Bruzzese R, Philip R and Amoruso S 2018 Direct femtosecond laser surface structuring of crystalline silicon at 400 nm Appl. Phys. Lett. 112 121601
[15] Gedvilas M, Voisiat B, Regelskis K and Račiukaitis G 2014 Impact of capillarity forces on the steady-state self-organization in the thin chromium film on glass under laser irradiation Thin Solid Films 571 102–7
[16] Regelskis K, Račiukaitis G and Gedvilas M 2007 Ripple formation in the chromium thin film during laser ablation Appl. Surf. Sci. 253 6584–7
[17] Gedvilas M, Voisiat B, Račiukaitis G and Regelskis K 2009 Self-organization of thin metal films by irradiation with nanosecond laser pulses Appl. Surf. Sci. 255 9826–9
[18] Zhang D S and Sugioka K 2019 Hierarchical microstructures with high spatial frequency laser induced periodic surface structures possessing different orientations created by femtosecond laser ablation of silicon in liquids Opt. Electron. Adv. 2 190002
[19] Cheng H C, Li P, Liu S, Chen P, Han L, Zhang Y, Hu W and Zhao J L 2017 Vortex-controlled morphology conversion of microstructures on silicon induced by femtosecond vector vortex beams Appl. Phys. Lett. 111 141901
[20] Jj Nivas J, He S T, Song Z M, Rubano A, Vecchione A, Paparo D, Marrucci L, Bruzzese R and Amoruso S 2017 Femtosecond laser surface structuring of silicon with Gaussian and optical vortex beams Appl. Surf. Sci. 418 565–71
[21] Ouyang J, Perrie W, Allegre O J, Heil T, Jin Y, Fearon E, Eckford D, Edwardson S P and Dearden G 2015 Tailored optical vector fields for ultrashort-pulse laser induced complex surface plasmon structuring Opt. Express 23 12562–72

[22] Zhang D S, Ranjan B, Tanaka T and Sugikoa K 2020 Underwater persistent bubble-assisted femtosecond laser ablation for hierarchical micro/nano-structuring Int. J. Extreme Manuf. 2 015001

[23] Zhang D S, Wu L C, Ueki M, Ito Y and Sugikoa K 2020 Femtosecond laser shockwave peening ablation in liquids for hierarchical micro/nanostructuring of brittle silicon and its biological application Int. J. Extreme Manuf. 2 044501

[24] Qiao H Z, Yang J J, Li J, Liu Q, Liu J and Guo C L 2018 Formation of subwavelength periodic triangular arrays on tungsten through double-pulsed femtosecond laser irradiation Materials 11 2380

[25] Liu Q, Zhang N, Yang J J, Qiao H Z and Guo C L 2018 Direct fabricating large-area nanotriangle structure arrays on tungsten surface by nonlinear lithography of two femtosecond laser beams Opt. Express 26 11718–27

[26] Zheng X, Zhao B, Yang J J, Lei Y H, Zou T T and Guo C L 2020 Noncollinear excitation of surface plasmons for triangular structure formation on Cr surfaces by femtosecond lasers Appl. Surf. Sci. 507 144932

[27] Jalil S A, Yang J J, ElKabbash M, Cong C and Guo C L 2019 Formation of controllable 1D and 2D periodic surface structures on cobalt by femtosecond double pulse laser irradiation Appl. Phys. Lett. 115 031601

[28] Romano J M, Helbig R, Fraggelakis F, Garcia-Giron A, Werner C, Kling R and Dimov S 2019 Springtail-inspired triangular laser-induced surface textures on metals using MHz ultrashort pulses J. Micro Nano-Manuf. 7 024504

[29] Romano J M, Garcia-Giron A, Penchev P and Dimov S 2018 Triangular laser-induced submicron textures for functionalising stainless steel surfaces Appl. Surf. Sci. 440 162–9

[30] Giannuzzi G, Gaudioso C, di Mundo R, Mirenghi L, Fraggelakis F, Kling R, Lugarà F M and Ancona A 2019 Short and long term surface chemistry and wetting behaviour of stainless steel with 1D and 2D periodic structures induced by bursts of femtosecond laser pulses Appl. Surf. Sci. 494 1055–65

[31] Fraggelakis F, Minuzzi G, Lopez J, Maneck-Hönninger I and Kling R 2019 Controlling 2D laser nano structuring over large area with double femtosecond pulses Appl. Surf. Sci. 470 677–86

[32] van der Poel S H, Mezera M, Römer G W R B E, de Vries E G and Matthews D T A 2019 Fabricating laser-induced periodic surface structures on medical grade cobalt–chrome–molybdenum: tribological, wetting and leaching properties Lubrificants 7 70

[33] Cross M C and Hohenberg P C 1993 Pattern formation outside of equilibrium Rev. Mod. Phys. 65 851–1112

[34] Kuznetsov A I, Koch J and Chichkov B N 2009 Nanostructuring of thin gold films by femtosecond lasers Appl. Phys. A 94 221–30

[35] Ivanov D S, Lin Z B, Rethfeld B, O’Connor G M, Glynn T J and Zhigilei L V 2010 Nanocrystalline structure of nanobump generated by localized photoexcitation of metal film J. Appl. Phys. 107 013519

[36] Fang M, Chandra S and Park C B 2008 Building three-dimensional objects by deposition of molten metal droplets Rapid Prototyp. J. 14 44–52

[37] Li H J, Wang P Y, Qi L H, Zuo H S, Zhong S Y and Hou X H 2012 3D numerical simulation of successive deposition of uniform molten Al droplets on a moving substrate and experimental validation Comput. Mater. Sci. 65 291–301

[38] Yi H, Qi L H, Luo J, Zhang D C, Li H J and Hou X H 2018 Effect of the surface morphology of solidified droplet on remelting between neighboring aluminum droplets Int. J. Mach. Tools Manuf. 130–131 1–11

[39] Keiser L, Bense H, Colinet P, Bico J and Reyssat E 2017 Marangoni bursting: evaporation-induced emulsification of binary liquids on a mixture layer Phys. Rev. Lett. 118 074504

[40] Bashir S, Rafique M S, Nathala C S and Husinsky W 2014 The formation of nanodimensional structures on the surface of thin exposed to femtosecond laser pulses in the ambient environment of ethanol Appl. Surf. Sci. 290 53–8

[41] Wu H et al 2019 Large area metal micro-/nano-groove arrays with both structural color and anisotropic wetting fabricated by one-step focused laser interference lithography Nanoscale 11 4803–10

[42] Zhang D S, Chen F, Fang G P, Yang Q, Xie D G, Qiao J G, Li W, Si J H and Hou X 2010 Wetting characteristics on hierarchical structures patterned by a femtosecond laser J. Micromech. Microeng. 20 075029

[43] Zhu S W et al 2020 High performance bubble manipulation on ferrofluid-infused laser-ablated microstructured surfaces Nano Lett. 20 5513–21

[44] Zhu S W, Bian Y C, Wu T, Li E Q, Li J W, Hu Y L, Wu D and Chu J R 2020 Spontaneous and unidirectional transportation of underwater bubbles on superhydrophobic dual rails Appl. Phys. Lett. 116 093706

[45] Lv X D, Jiao Y L, Wu S Z, Li C Z, Zhang Y Y, Li J W, Hu Y L and Wu D 2019 Anisotropic sliding of underwater bubbles on microgrooved slippery surfaces by one-step femtosecond laser scanning ACS Appl. Mater. Interfaces 11 20574–80

[46] Sedao X et al 2016 Growth swimming and generation of high-frequency surface nanostructures in ultrafast laser-induced transient melting and resolidification ACS Nano 10 6995–7007

[47] Hou S S, Huo Y X, Xiong P X, Zhang Y, Zhang S A, Jia T Q, Sun Z R, Qiu J R and Xu Z Z 2011 Formation of long- and short-periodic nanoripples on stainless steel irradiated by femtosecond laser pulses J. Phys. D: Appl. Phys. 44 505401

[48] Liu R J, Zhang D S and Li Z G 2021 Femtosecond laser induced simultaneous functional nanomaterial synthesis, in situ deposition and hierarchical LIPSS nanostructuring for tunable antireflectance and iridescence applications J. Mater. Sci. Technol. 89 179–85

[49] Zhang D S, Göckbe B and Barckwiosk S 2017 Laser synthesis and processing of colloids: fundamentals and applications Chem. Rev. 117 3990–4103

[50] Ishikawa Y, Shimizu Y, Sasaki T and Koshizaki N 2006 Preparation of zinc oxide nanorods using pulsed laser ablation in water media at high temperature J. Colloid Interfaces Sci. 300 612–5

[51] Xie X Z, Zhou C X, Wei X, Hu W and Ren Q L 2019 Laser machining of transparent brittle materials: from machining strategies to applications Opt. Electron. Adv. 2 180017

[52] Yu P, Besteirote L Y, Huang Y J, Wu Y, Fu L, Tan H H, Jagadish C, Wiederrecht G P, Govorov A O and Wang Z M 2019 Broadband metamaterial absorbers Adv. Opt. Mater. 7 1800995

[53] Wang J, Shen Z X, Wu W and Feng K M 2015 Wideband circular polarizer based on dielectric gratings with periodic parallel strips Opt. Express 23 12533–43

[54] Pan M Y, Li Q, Hong Y, Cai L, Lu J and Qiu M 2018 Circular-polarization-sensitive absorption in refractory metamaterials composed of molybdenum zigzag arrays Opt. Express 26 17772–80

[55] Shih C Y, Gnilitskiy I, Shugaev M V, Skoulas E, Stratakis E and Zhigilei L V 2020 Effect of a liquid environment
on single-pulse generation of laser induced periodic surface structures and nanoparticles Nanoscale 12 7674–87

[56] Skoulas E, Tasolamprou A C, Kenanakis G and Stratakis E 2020 Laser induced periodic surface structures as polarizing optical elements Appl. Surf. Sci. 541 148470

[57] Murphy R D, Torralva B, Adams D P and Yalisove S M 2013 Laser-induced periodic surface structure formation resulting from single-pulse ultrafast irradiation of Au microstructures on a Si substrate Appl. Phys. Lett. 102 211101

[58] Xue H Y, Deng G L, Feng G Y, Chen L, Li J Q, Yang C and Zhou S H 2017 Role of nanoparticles generation in the formation of femtosecond laser-induced periodic surface structures on silicon Opt. Lett. 42 3315–8

[59] Öktem B, Pavlov I, Ilday S, Kalaycıoglu H, Rybak A, Yavaş S, Erdögan M and Ilday F Ö 2013 Nonlinear laser lithography for indefinitely large-area nanostructuring with femtosecond pulses Nat. Photon. 7 897–901

[60] Li X F, Zhang C Y, Li H, Dai Q F, Lan S and Tie S L 2014 Formation of 100 nm periodic structures on a titanium surface by exploiting the oxidation and third harmonic generation induced by femtosecond laser pulses Opt. Express 22 28086–99

[61] Qiao H Z, Yang J J, Wang F, Yang Y and Sun J L. 2015 Femtosecond laser direct writing of large-area two-dimensional metallic photonic crystal structures on tungsten surfaces Opt. Express 23 26617–27

[62] Yoon H J, Bang K S, Lim J W and Lee S Y 2016 Optical properties of zirconium oxide thin films for semitransparent solar cell applications J. Mater. Sci., Mater. Electron. 27 11358–65

[63] Livakas N, Skoulas E and Stratakis E 2020 Omnidirectional iridescence via cylindrically-polarized femtosecond laser processing Opt. Electron. Adv. 3 190035

[64] Qian J and Zhao Q Z 2020 Anti-counterfeiting microstructures induced by ultrashort laser pulses Phys. Status Solidi a 217 1901052

[65] Teutoburg-Weiss S, Sonntag F, Günther K and Lasagni A F 2019 Multiple method micromachining laser platform for fabricating anti-counterfeit elements with multiple-scaled features Opt. Laser Technol. 115 465–76

[66] Wu P C, Cao X W, Zhao L, Chen Z H, Zhang M N, Juodkazis S and Zhang W W 2021 Dynamic structural color display based on femtosecond laser variable polarization processing Adv. Mater. Interfaces 8 2100460

[67] Zhang Y C, Jiang Q L, Cao K Q, Chen T Q, Cheng K, Zhang S A, Feng D H, Jia T Q, Sun Z R and Qiu J R 2021 Extremely regular periodic surface structures in a large area efficiently induced on silicon by temporally shaped femtosecond laser Photonics Res. 9 839–47