

Article

Repetition Frequency-Dependent Formation of Oxidized LIPSSs on Amorphous Silicon Films

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Abstract

Laser-induced periodic surface structures (LIPSSs) produced via ultrafast laser-induced oxidation offer a promising route for high-quality nanostructuring, with reduced thermal damage compared to conventional ablation-based methods. However, the influence of laser repetition frequency on the formation and morphology of oxidized LIPSSs remains insufficiently explored. In this study, we systematically investigate the effects of varying the femtosecond laser repetition frequency from 1 kHz to 100 kHz while keeping the total pulse number constant on the oxidation-induced LIPSSs formed on amorphous silicon films. Scanning electron microscopy and Fourier analysis reveal a transition between two morphological regimes with increasing repetition frequency: at low frequencies, the long inter-pulse intervals result in irregular, disordered oxidation patterns; at high frequencies, closely spaced pulses promote the formation of highly ordered, periodic surface structures. Statistical measurements show that the laser-modified area decreases with frequency, while the LIPSS period remains relatively stable and the ridge width exhibits a peak at 10 kHz. Finite-difference time-domain (FDTD) and finite-element simulations suggest that the observed patterns result from a dynamic balance between light-field modulation and oxidation kinetics, rather than thermal accumulation. These findings advance the understanding of oxidation-driven LIPSS formation dynamics and provide guidance for optimizing femtosecond laser parameters for precise surface nanopatterning.

Keywords: oxidized LIPSSs; repetition frequency; amorphous silicon



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1. Introduction

Laser-induced periodic surface structures (LIPSSs) are spontaneously formed nano- and microscale ripple patterns produced by intense laser irradiation of solid surfaces. Initially observed by Birnbaum in 1965 [1], LIPSSs have drawn substantial research interest, especially following the emergence of femtosecond laser systems [2–4]. These structures provide a straightforward, single-step method to fabricate large-area periodic nanostructures beyond the optical diffraction limit [5], applicable to various materials including metals [6–9], semiconductors [10–14], and dielectrics [15,16]. Such textured surfaces have demonstrated significant utility in numerous applications spanning optics [17–19], photon-

ics [20,21], tribology [22–24], biology [25–27], and medicine [28–30], primarily due to their customizable surface properties.

LIPSSs are most frequently formed through ablation-based mechanisms, where periodic energy deposition and material removal are often attributed to near-surface electromagnetic interference effects. In particular, in conductive materials such as metals, the interference between incident laser fields and surface electromagnetic modes—including surface plasmon polaritons (SPPs)—can lead to spatially modulated absorption that promotes periodic ablation under suitable fluence conditions [31]. While this approach has been widely studied, it often yields irregular or discontinuous patterns due to the stochastic nature of ablation processes—such as ripple bifurcation, branching, debris formation, and residual heat accumulation [32]. To address these limitations, recent studies have explored ultrafast laser-induced surface oxidation at fluences well below the ablation threshold [33–37]. This oxidation-based regime significantly reduces thermal damage and suppresses debris generation, enabling the fabrication of highly regular, well-defined periodic oxide structures.

In contrast to conventional ablation-based LIPSSs, oxidized LIPSSs formed on amorphous silicon (a-Si) surfaces offer a particularly promising alternative, owing to their distinct formation mechanism and superior structural regularity. Geng et al. recently introduced the Optical Localization-Induced Nonlinear Competition (O-LINC) mechanism [36], in which an initially oxidized nanoparticle acts as a dominant seed, enhancing localized electric fields and guiding the anisotropic growth of ripple structures along the laser polarization direction. Complementing this, the quasi-cylindrical wave (QCW) model describes how scattered electromagnetic fields from these seed particles interfere with the incident light, reinforcing periodicity in the surrounding regions [38]. Together, these mechanisms constitute a coherent theoretical framework that distinguishes oxidation-driven LIPSSs from their ablation-based counterparts, and explain their enhanced order, uniformity, and reproducibility.

While oxidation-induced LIPSSs offer a promising route for fabricating high-quality periodic nanostructures, the formation process is influenced by a multitude of laser parameters—including pulse energy [39], polarization [35,40], film thickness [34], and scanning speed [11,41]—which have been extensively studied. However, the specific role of laser repetition frequency remains comparatively underexplored, despite its critical influence on the thermal and chemical environment between successive pulses. Most existing studies that touch on repetition frequency focus primarily on heat accumulation effects, often in metallic or crystalline materials [42]. In contrast, few investigations have systematically isolated the impact of repetition frequency on LIPSS formation under conditions where heat accumulation is minimized. To fill this knowledge gap, as shown in Figure 1, the present study examines how varying the femtosecond laser repetition frequency—from 1 kHz to 100 kHz regimes—while keeping the total pulse count constant affects the morphology and oxidation behavior of LIPSSs formed on amorphous silicon films.

At higher frequencies, the shortened inter-pulse interval limits the available time for surface oxidation, suppressing random multi-nucleation and favoring orderly ridge growth guided by near-field enhancement. Conversely, lower frequencies extend the oxidation window, allowing more dispersed nucleation and leading to less regular structures. By disentangling the effects of frequency from cumulative energy input, we aim to clarify the interplay between transient oxidation kinetics and optical field modulation, ultimately enabling more precise control over oxidized LIPSSs.

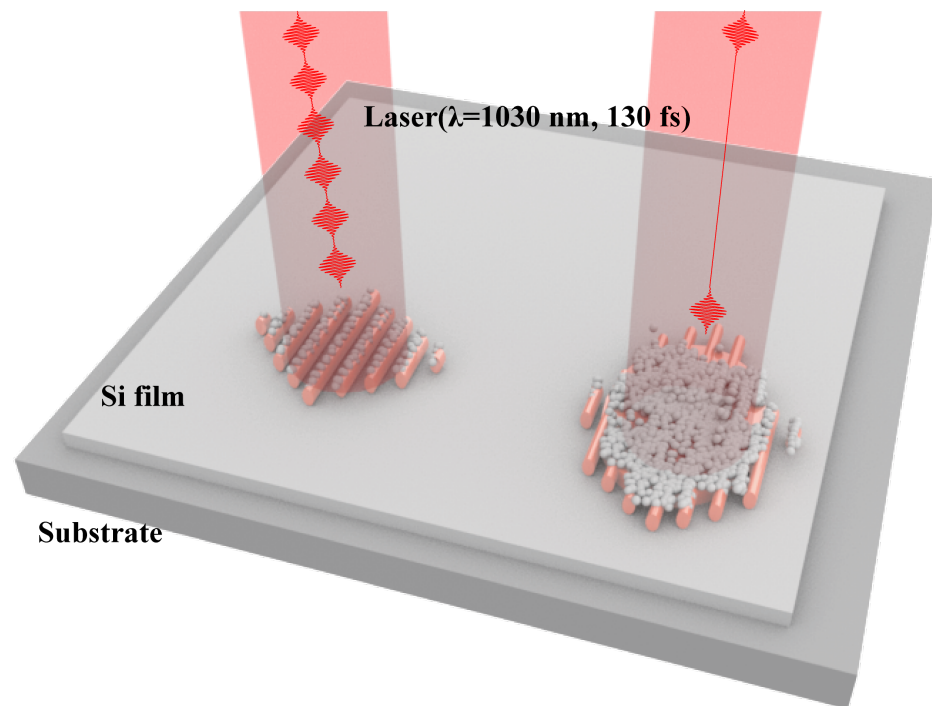


Figure 1. Schematic of the experimental approach. A 1030 nm, 130 fs laser irradiates a 200 nm-thick amorphous silicon film under different repetition frequencies. The inter-pulse interval, governed by repetition frequency, critically affects oxidation dynamics and laser induced periodic surface structures (LIPSSs) ordering: short intervals (high frequency) suppress random nucleation, while long intervals (low frequency) promote disordered growth.

2. Materials and Methods

2.1. Experimental Setup

Femtosecond laser processing experiments were performed using a diode-pumped ultrafast fiber amplifier system (Amplitude, Pessac, France), delivering pulses of 130 fs duration at a central wavelength of 1030 nm. The laser beam was guided through a galvanometric scanner (Han's, Shenzhen, China) and loosely focused onto the sample surface using a field lens. The resulting laser spot diameter was approximately 67 μm , characterized using a laser beam profiler (Ophir Photonics, Jerusalem, Israel).

The laser repetition frequency was controlled via the internal software interface provided by the laser manufacturer. The system employs an integrated pulse picker and modulator, enabling direct user adjustment of the pulse frequency through the synchronization control panel, ensuring stable and synchronized pulse delivery.

Laser fluence was adjusted using a combination of a half-wave plate and a polarizer. The average laser power was monitored using a calibrated photodiode power sensor (Thorlabs, Newton, NJ, USA). A fast electronic shutter (DHC, Beijing, China) was incorporated into the optical path to precisely control irradiation time and ensure accurate pulse delivery.

During experiments, the samples were mounted on a stationary platform, and all laser exposures were conducted under ambient laboratory conditions with the laser incident normally (perpendicular) to the sample surface.

All experiments were performed in a cleanroom environment at a measured temperature of 25 $^{\circ}\text{C}$ and a relative humidity of approximately 40%. The atmosphere was standard laboratory air with an oxygen concentration of 21%.

2.2. Sample Preparation

Amorphous silicon (a-Si) thin films with a thickness of approximately 200 nm were deposited onto 2-inch single-crystalline silicon wafers using a magnetron sputtering system (ULVAC Inc., Kanagawa, Japan) at room temperature. RF sputtering was employed with a power of 300 W under an argon atmosphere at a pressure of 0.3 Pa. The argon flow rate was maintained at 70 sccm, and the target-to-substrate distance was set at 90 mm. Film thickness was measured using a stylus profilometer (KLA-Tencor, Milpitas, CA, USA).

2.3. Surface Characterization

Surface morphology was characterized using a field-emission scanning electron microscope (Zeiss) operated at 3 kV, with magnifications ranging from 900× to 25,000×. The laser-modified areas were extracted from SEM images by manual thresholding in the Fiji software, while the LIPSSs' periods and ridge widths were measured directly based on the scale bar. To further evaluate the spatial coherence of the structures, two-dimensional fast Fourier transforms (2D FFTs) were performed using MATLAB R2022b, and the dispersion of the LIPSS orientation angles (DLOA) was quantified from the angular distribution of the dominant spatial frequencies.

2.4. Numerical Simulations

In the FDTD simulations, a multilayer structure was constructed to replicate the experimental configuration, consisting of a 200 nm-thick amorphous silicon (a-Si) film atop a 1180 nm-thick crystalline silicon (c-Si) substrate. To emulate early-stage oxidation nuclei or surface impurities, a single SiO₂ nanoparticle with a radius of 150 nm was embedded within the a-Si layer. This particle size reflects the typical lateral dimensions of isolated oxidized features observed in our SEM images. Similar size ranges have also been reported in prior studies to induce strong near-field enhancement during femtosecond laser irradiation on silicon surfaces [43]. A linearly polarized monochromatic plane wave with a wavelength of 1030 nm was normally incident on the sample surface, with the polarization direction aligned parallel to the x-axis. To capture the near-field intensity distribution, a power monitor was positioned just above the surface. Simulations were performed over a total duration of 1000 fs, and convergence was confirmed when the auto shutoff level fell below the predefined threshold of 10^{-5} .

For thermal modeling, COMSOL Multiphysics 6.2 was used with the same geometrical configuration. A Gaussian transient heat source with a diameter of 67 µm was applied to the surface to simulate the energy deposition from a single laser pulse. The transient heat transfer module was employed, incorporating thermal conduction into the underlying substrate. Material properties for a-Si, c-Si, and SiO₂ were adopted from literature values. The simulations captured the time evolution of the surface temperature to evaluate the cooling dynamics after femtosecond laser excitation.

A detailed summary of the material parameters and boundary conditions used in both the FDTD and COMSOL simulations is provided in the Supplementary Materials.

3. Results

3.1. Morphology Evolution

Figure 2 presents the morphological evolution of an amorphous silicon (a-Si) thin-film surface following femtosecond laser irradiation at repetition frequencies ranging from 1 kHz to 100 kHz, while maintaining a constant pulse count of 40,000. All experiments were performed under identical conditions—including a wavelength of 1030 nm, pulse duration of 130 fs, and single-pulse energy of 6 µJ—to isolate the influence of repetition frequency on surface morphology.

The results reveal a distinct transition between two morphological regimes as the repetition frequency increases. At lower frequencies (1–10 kHz), surface modification is predominantly governed by disordered oxidation, while higher frequencies (20–100 kHz) favor the formation of well-ordered laser-induced periodic surface structures.

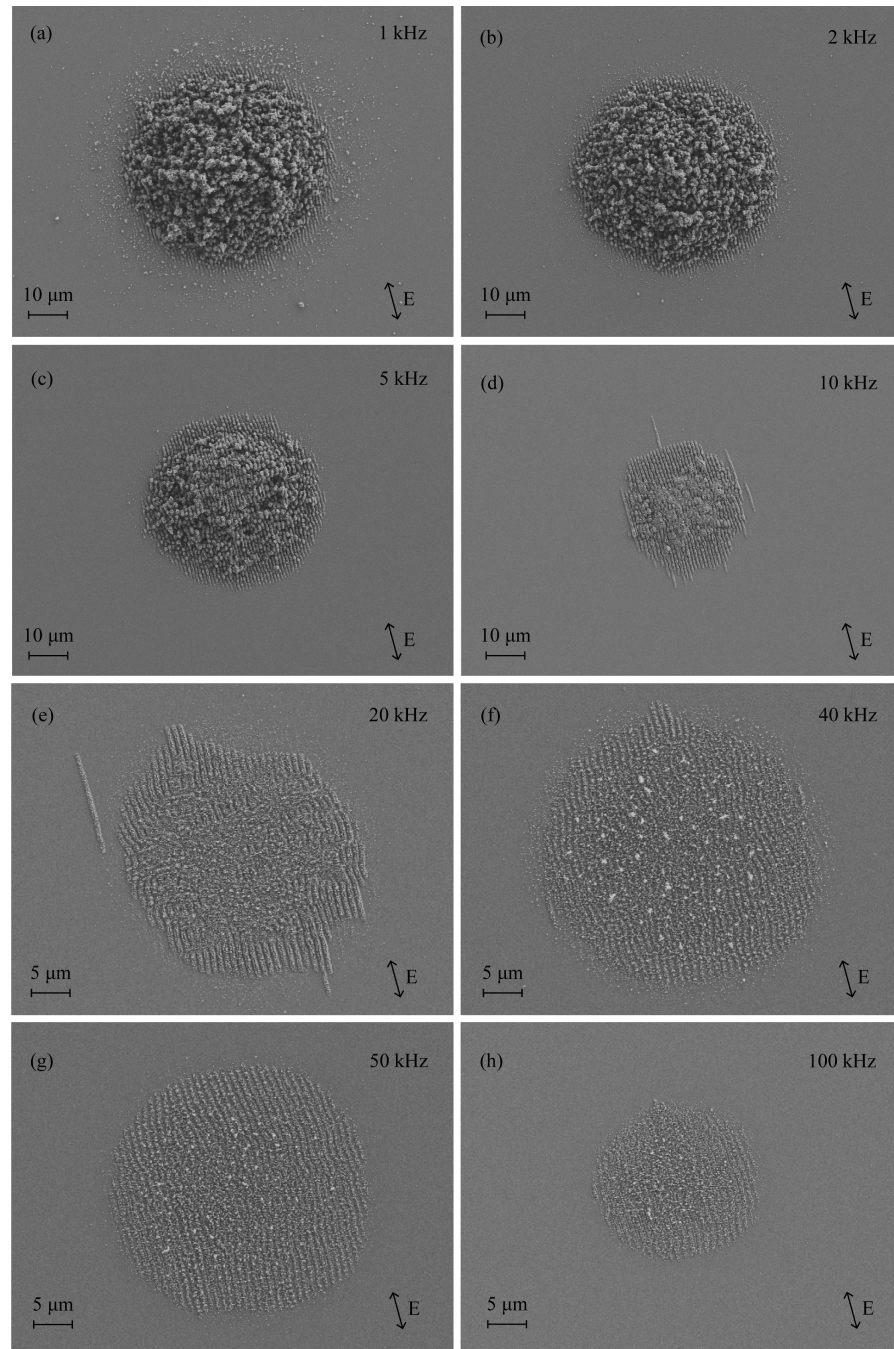


Figure 2. SEM images illustrating the morphological evolution of the amorphous silicon thin-film surface after irradiation with a constant total of 40,000 femtosecond laser pulses at different repetition frequencies. Panels (a–d) correspond to the oxidation-dominated regime (1–10 kHz), where disordered oxide clusters prevail and only faint, incoherent LIPSSs are observed. Panels (e–h) represent the periodic-structuring regime (20–100 kHz), characterized by spatially ordered, ripple-like oxidized LIPSSs. All surface features are attributed to laser-induced oxidation, with the repetition frequency modulating their spatial coherence and morphology. Scale bar: 10 μm. The $\vec{E}$ denotes the polarization direction of the incident laser.

Regime I: Disordered oxidation-dominated morphology (1–10 kHz). At the lowest frequencies (1–2 kHz, Figure 2a,b), the surface is dominated by large clusters of randomly distributed oxidized particles, primarily concentrated in the central region of the laser-affected zone. These irregular features result from prolonged oxidation reactions driven by the long inter-pulse intervals. Faint and partially developed LIPSSs begin to emerge near the periphery, but remain spatially incoherent and visually obscured by the central oxidation zone. As the frequency increases to 5–10 kHz (Figure 2c,d), a transitional morphology appears. The central oxidation zone shrinks significantly, and periodic structures become more apparent and widespread. However, a residual oxidized core remains, indicating that random oxidation still plays a non-negligible role.

Regime II: LIPSS-dominated morphology (20–100 kHz). At higher repetition frequencies (20–50 kHz, Figure 2e–g), the influence of disordered oxidation diminishes substantially. The irradiated surfaces are increasingly covered by continuous, well-aligned LIPSSs, exhibiting high spatial regularity and extended lateral coherence. Only sparse traces of oxidized particles remain, mostly confined to the very center of the irradiation zone. At 100 kHz (Figure 2h), the transition is complete. The surface morphology consists exclusively of uniform, periodic LIPSSs with no observable central oxidation clusters. These results confirm that closely spaced laser pulses promote spatially coherent periodic structuring and suppress stochastic oxidation dynamics.

Overall, the observed morphological evolution suggests that the repetition frequency governs a transition between two oxidation-driven regimes. At low frequencies, the surface is dominated by widespread, disordered oxidation with no spatial coherence, while at high frequencies, the oxidation process becomes spatially modulated, giving rise to highly ordered, periodic LIPSSs.

3.2. Structural Analysis

To elucidate the internal structural organization at low repetition frequencies (1–10 kHz), the irradiated region was spatially divided into two distinct morphological zones: a central oxidation zone (COZ) and a peripheral LIPSS zone (LZ), as illustrated in Figure 3a. The COZ, situated at the beam center, is dominated by disordered oxide nanoparticles lacking clear periodicity. In contrast, the LZ comprises periodic, ridge-like oxidized LIPSSs localized near the periphery. These distinct morphologies arise from the Gaussian energy distribution of the femtosecond laser beam (Figure 3b): the central region experiences excessive fluence, leading to over-oxidation and loss of spatial coherence, whereas the periphery receives moderate fluence levels that support field-guided, periodic oxidation.

Such spatial segregation is a hallmark of the disordered oxidation-dominated regime, characteristic of low-frequency laser processing. Although both disordered oxidation and periodic modulation coexist in this regime, they are highly localized and morphologically decoupled. As the repetition frequency increases beyond 10 kHz, this behavior transitions into a distinct periodic-structuring regime. Here, the COZ progressively shrinks and eventually disappears, while the LZ expands to dominate the entire irradiated region. At frequencies above 20 kHz, spatially coherent ripple structures uniformly cover the modified area, indicating that field-guided oxidation becomes the prevailing mechanism.

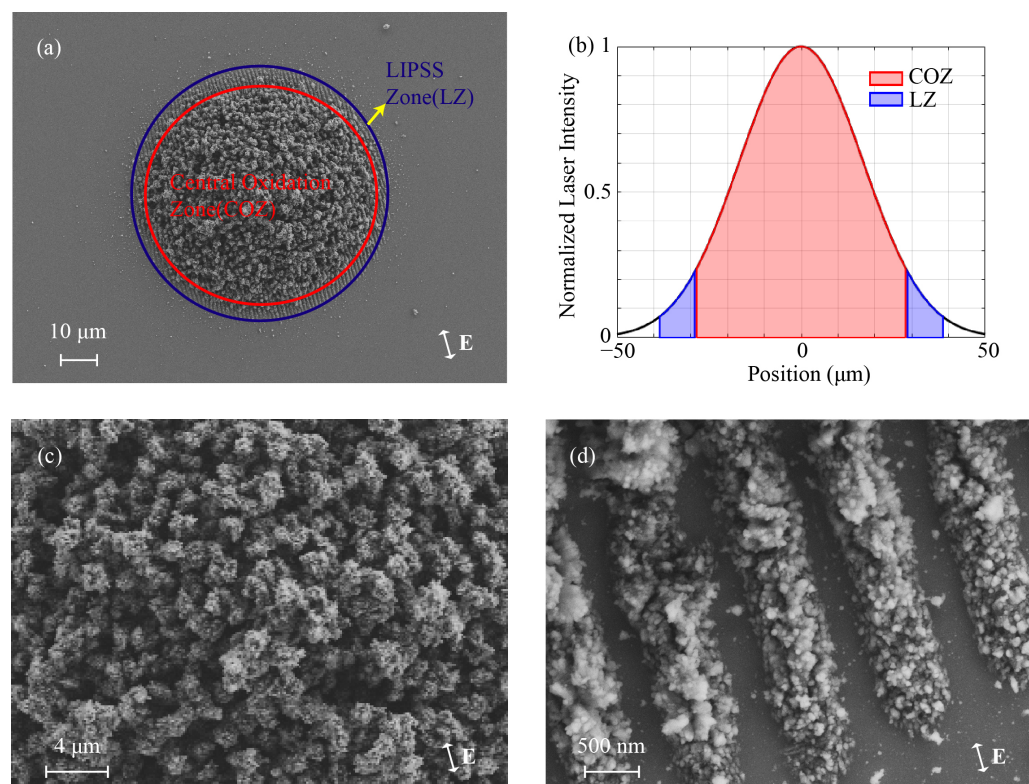


Figure 3. Spatial division and morphological features of the irradiated area at 2 kHz repetition frequency. (a) SEM image showing the central oxidation zone (COZ) and peripheral LIPSS zone (LZ), overlaid with colored boundaries. (b) Gaussian intensity distribution of the laser spot, indicating relative energy fluence received by the COZ and LZ. (c) High-magnification SEM of the COZ, showing disordered oxidized particle accumulation. (d) High-magnification SEM of the LZ, revealing ridge-like oxidized LIPSSs aligned parallel to the laser polarization direction $\vec{E}$.

To quantitatively characterize the transition between the two morphological regimes, we performed a two-dimensional fast Fourier transform (2D FFT) analysis of the SEM images in Figure 2. The resulting frequency-domain spectra are summarized in Figure 4 and reveal distinct features associated with each regime. In the disordered oxidation-dominated regime (1–10 kHz), the FFT spectra exhibit broad, isotropic noise without discernible peaks, indicating the absence of periodic surface order. This corresponds to a surface morphology governed by disordered oxidation, lacking coherent field modulation. At 10 kHz—near the transition boundary—weak but symmetric peaks begin to emerge, marking the onset of periodic structuring. In the periodic-structuring regime (20–100 kHz), the FFT patterns display well-defined, directional peaks, reflecting increasingly regular and coherent LIPSS formation. As frequency increases, the peaks become sharper and more localized, signifying enhanced spatial order. At 100 kHz, the FFT peaks remain tightly focused, although slightly reduced in intensity, suggesting diminished oxidation depth despite high structural regularity.

To further assess ripple alignment, we calculated the dispersion of the LIPSS orientation angle (DLOA), a quantitative metric that reflects the spread in ripple directions and serves as an indicator of structural coherence [44], as summarized in Table 1. In the disordered oxidation regime (1–5 kHz), DLOA values could not be reliably extracted due to the absence of periodic features in the Fourier domain. At 10 kHz, the DLOA reaches a sharp minimum of 9.43° , indicating a critical transition point between random and ordered surface morphology. This transition marks the onset of coherent LIPSS formation and the boundary between the two regimes. In the periodic LIPSS regime (20–100 kHz), the DLOA initially increases to 25.17° at 20 kHz, indicating a temporary decrease in LIPSS orientation uniformity. This is likely due to the inter-pulse interval (50 μs) entering a transitional

regime—shorter than low-frequency conditions that allow for extensive random nucleation, but not yet short enough for full dominance of optical near-field-guided ordering. Consequently, both mechanisms coexist and compete, leading to local disorder and increased angular deviation. At higher frequencies, the DLOA decreases again, reaching 4.90° at 100 kHz, reflecting enhanced alignment as closely spaced pulses stabilize ripple orientation. This non-monotonic variation highlights the significance of repetition frequency in modulating structural order during laser-induced oxidation.

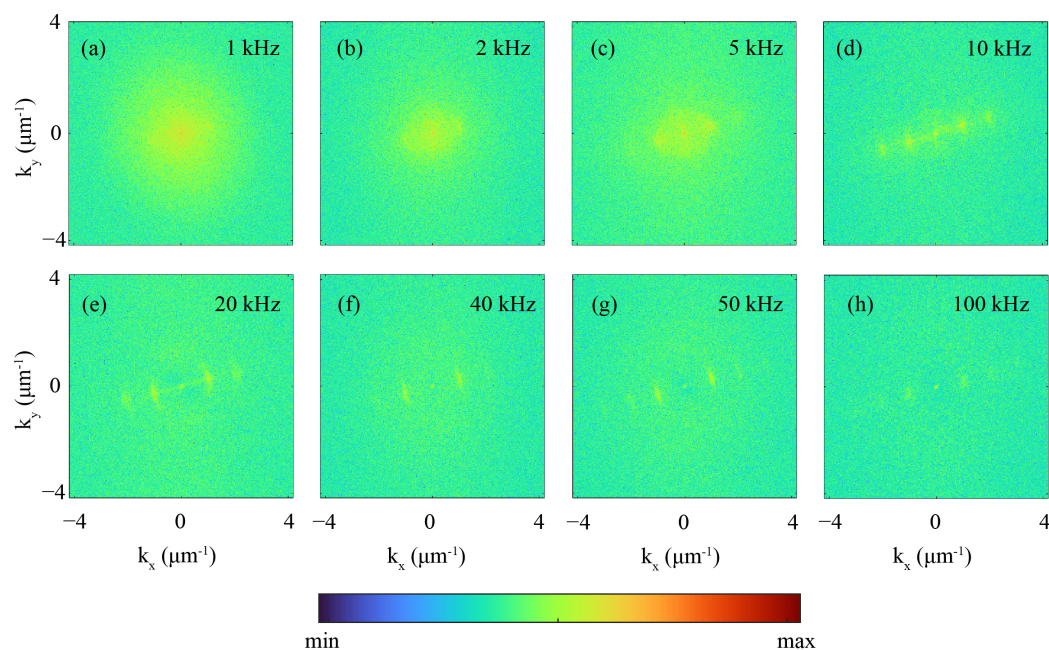


Figure 4. Two -dimensional fast Fourier transform (2D FFT) maps of SEM images at various repetition frequencies: (a) 1 kHz, (b) 2 kHz, (c) 5 kHz, (d) 10 kHz, (e) 20 kHz, (f) 40 kHz, (g) 50 kHz, and (h) 100 kHz. The frequency-domain maps reflect the spatial regularity of the laser-induced surface structures. At low repetition frequencies (1–5 kHz), the FFTs exhibit diffused, isotropic noise due to disordered oxidation. At 10 kHz, distinct peaks emerge, indicating highly ordered LIPSS formation. As the frequency increases further, peak sharpness and symmetry generally improve, although intensity weakens due to decreasing modulation depth.

Table 1. Dispersion of LIPSS orientation angle (DLOA) at different laser repetition frequencies.

Repetition Frequency (kHz)	DLOA ($^\circ$)	Morphological Regime
1	N/A	Disordered oxidation-dominated
2	N/A	Disordered oxidation-dominated
5	N/A	Disordered oxidation-dominated
10	9.43	Disordered oxidation-dominated (transition point)
20	25.17	LIPSS-dominated
40	18.38	LIPSS-dominated
50	17.15	LIPSS-dominated
100	4.90	LIPSS-dominated

3.3. Morphological Metrics

To quantitatively assess the influence of repetition frequency on laser-induced surface modification, we evaluated three key morphological parameters: the total modified area, the LIPSSs' period, and the ridge width of the oxidized structures, as summarized in Figure 5.

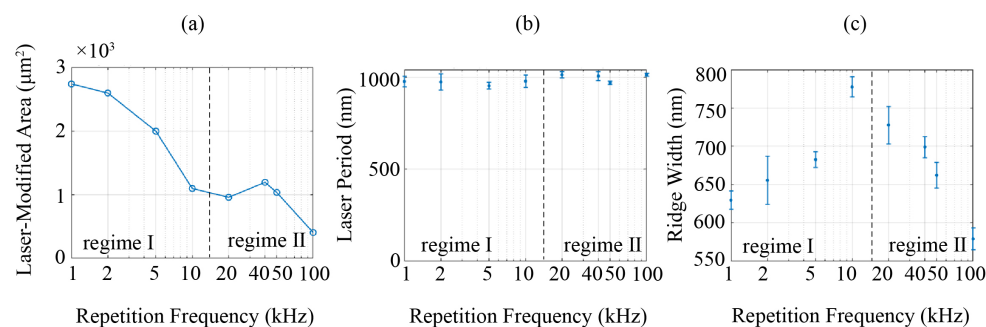


Figure 5. Quantitative analysis of surface morphological parameters as a function of laser repetition frequency. The vertical dashed line indicates the transition between the disordered oxidation-dominated regime (regime I, 1–10 kHz) and the LIPSS-dominated regime (regime II, 20–100 kHz). (a) Laser-modified area extracted from binarized SEM images, showing an overall decreasing trend due to shortened oxidation time, with a local increase near the regime boundary. (b) LIPSS period remains relatively stable across the full frequency range. (c) Ridge width of oxidized LIPSSs, which peaks at 10 kHz and decreases at higher frequencies, reflecting the transition from extended oxidation to more confined stripe growth. Error bars represent standard deviations from multiple measurements.

The spatial extent of modification (Figure 5a) was determined from SEM images using the Fiji software by applying a uniform binarization threshold. As the total pulse number is held constant, increasing the repetition frequency reduces the total irradiation duration, leading to an overall decrease in the modified area as frequency increases from 1 kHz to 100 kHz. In the disordered oxidation-dominated regime (1–10 kHz), longer inter-pulse intervals facilitate sustained oxidation and lateral growth, resulting in broader affected regions. In contrast, the LIPSS-dominated regime (20–100 kHz) exhibits more confined modification zones due to limited oxidation time.

Interestingly, the data shows a local increase in modified area at 40 kHz, deviating from the overall decreasing trend. Notably, within the intermediate frequency range (10–50 kHz), the reduction in area becomes significantly less steep compared to the rapid drop observed in the low-frequency regime. This plateau-like behavior suggests a transitional region where no single mechanism dominates. As the system shifts from oxidation-driven growth to near-field-guided patterning, the competing effects of partial oxidation and field localization can introduce enhanced morphological variability. This local increase in area at 40 kHz may thus be interpreted as a manifestation of stochastic oxidation dynamics in the transitional regime.

The LIPSS period, shown in Figure 5b, was obtained by manually measuring the spacing between adjacent ridges in multiple SEM images and averaging the results. The period remains nearly constant across all frequencies, ranging from 971 nm to 1015 nm. This range is consistent with LIPSS periods reported in previous studies using similar wavelengths and material systems [34,36,38], falling within expected experimental variation. This consistency confirms that the periodicity is predominantly determined by the laser wavelength and the interference of scattered electromagnetic fields at the material surface, rather than by thermal accumulation or strongly frequency-dependent oxidation dynamics.

Figure 5c shows the average ridge width of the oxidized LIPSSs. The width increases with repetition frequency, peaking at approximately 785 nm at 10 kHz, and subsequently decreasing to around 580 nm at 100 kHz. This non-monotonic behavior reflects the transition between two distinct morphological regimes. In the disordered oxidation-dominated regime (1–10 kHz), the ridge width increases as disordered nanoparticle oxidation gives way to increasingly coherent LIPSS formation. Higher repetition frequencies in this range enhance energy deposition uniformity, favoring stripe-like growth over random accumulation. This transition aligns with the observed shrinkage of the central oxidation zone (COZ)

and the expansion of the peripheral LIPSSs zone (LZ), as supported by the 2D FFT results. In the LIPSS-dominated regime (20–100 kHz), although the optical field continues to guide periodic structuring, the significantly reduced oxidation time restricts material buildup, resulting in narrower ridges.

These quantitative results corroborate the previously discussed morphological trends and provide a comprehensive view of how surface structures evolve under varying repetition frequencies. The observed variations in modified area, ridge width, and periodicity reflect a complex interplay between pulse delivery rate, oxidation kinetics, and electromagnetic field modulation—parameters that are essential for the precise control of femtosecond laser-induced surface patterning.

3.4. Formation Dynamics

The morphological evolution of oxidized LIPSSs is governed by a dynamic balance between two interrelated factors: the modulation frequency of the femtosecond laser field and the effective oxidation duration during exposure. Higher repetition frequencies enhance directional ridge formation by providing frequent modulation cues, promoting anisotropic growth of oxidation seeds along the electric field polarization. However, for a fixed pulse number, increasing repetition frequency shortens the total oxidation time, thereby limiting the extent of oxide growth. Conversely, longer oxidation durations at lower frequencies allow for more oxidized particles to form, increasing the likelihood of multiple nucleation events. Furthermore, the reduced modulation frequency weakens the light field's ability to guide anisotropic growth. The optimal LIPSS morphology thus results from a balance between oxidation duration and light field modulation.

To clarify the underlying mechanism, we refer to the Optical Localization-Induced Nonlinear Competition (O-LINC) framework proposed by Geng et al. [36], which describes the anisotropic growth of oxide nanoparticles into periodic ridges. In this model, laser-induced near-field enhancement around a seed particle promotes oxidation along the laser polarization direction. The interference of quasi-cylindrical waves originating from the seed reinforces the electric field in neighboring regions, guiding the emergence of adjacent ridges in a periodic manner [38]. This field-mediated feedback enables the growth of well-aligned LIPSSs from an initially dominant particle.

Figure 6a shows our FDTD simulation, illustrating the near-field distribution around a single oxide nanoparticle under femtosecond laser illumination. A strong electric field concentration is observed at the poles along the polarization direction, confirming the anisotropic field distribution proposed in the O-LINC model. This localized enhancement drives directional oxidation and ridge elongation. Although the pulse duration is only 130 fs, the spatial field enhancement around the particle imprints a patterned oxidation response aligned with the polarization direction. After the pulse, the laser field vanishes, and oxidation proceeds thermally and chemically. At low repetition frequencies, the long inter-pulse interval allows oxidation to continue in the absence of optical modulation, potentially resulting in uncontrolled or multi-nucleation growth. In contrast, at high repetition rates, modulation is reintroduced rapidly, reinforcing directional growth and favoring the formation of coherent LIPSS patterns.

Figure 6b presents our COMSOL simulation of transient thermal behavior. The results show that the surface temperature induced by each femtosecond pulse rises sharply but returns to room temperature within approximately 1 μ s. Since the shortest pulse interval in our experiments (at 100 kHz) is 10 μ s, there is sufficient time for complete thermal relaxation between pulses. This indicates that residual heat—defined as undissipated thermal energy that accumulates from pulse to pulse—is not present under our conditions. Previous studies have shown that residual heat can distort LIPSS morphology by promoting surface melting,

disrupting periodic field modulation, and degrading pattern regularity [32]. The absence of such thermal accumulation in our setup rules out this interference mechanism, confirming that the observed LIPSSs' quality variations are not caused by redundant heat effects.

Figure 6c,d compare oxidation dynamics at low (2 kHz) and high (100 kHz) repetition frequencies. At 2 kHz (Figure 6c), multiple oxidized particles appear after just 5 k pulses, initiating from many locations without sufficient modulation guidance. These particles grow in an uncoordinated fashion, eventually forming a disordered oxidation zone (COZ) at the center. The lack of frequent field-driven modulation and mutual interference among particles results in poor LIPSS quality.

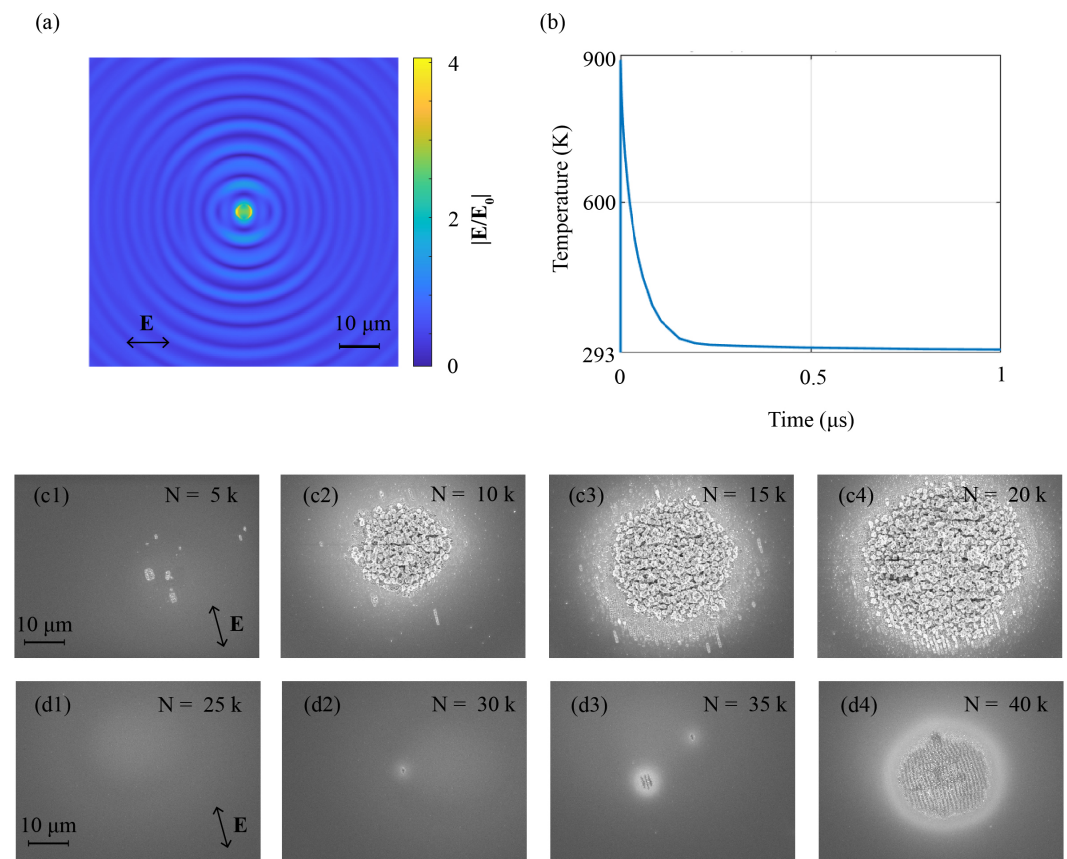


Figure 6. Simulation and experimental observations of oxidation dynamics at different repetition frequencies. (a) FDTD simulation showing near-field enhancement around a single oxide nanoparticle under femtosecond laser irradiation, with strong electric field localization along the polarization direction. (b) COMSOL simulation of surface temperature evolution, showing rapid thermal decay to room temperature within 1 μ s. (c1–c4) SEM images of oxidation evolution at 2 kHz with increasing pulse number (N, total pulses): early formation of multiple oxidation particles leads to disordered central oxidation zone (COZ). (d1–d4) Oxidation at 100 kHz: a single oxide seed appears at N = 30 k and grows into aligned LIPSS stripes by N = 40 k, with no COZ formation.

In contrast, at 100 kHz (Figure 6d), no oxidation is visible until 30 k pulses, at which point a single oxidized nanoparticle appears in the center of the irradiated area (Figure 6(d2)). This particle elongates under high-frequency modulation and, as shown in Figure 6(d3), induces the formation of adjacent ridges. By 40 k pulses (Figure 6(d4)), a coherent LIPSS pattern has emerged, with no central COZ. This behavior exemplifies the seed-dominated growth mechanism described by Geng et al., wherein a single oxidation site—amplified by near-field enhancement and optical feedback—governs the evolution of well-aligned LIPSSs. The high repetition rate ensures frequent modulation cues that reinforce directional growth

and suppress competing nucleation, ultimately leading to a steady-state stripe pattern with high structural coherence.

This comparison highlights the distinct formation mechanisms of LIPSSs under low and high repetition frequencies. At low frequencies, the long interval between pulses allows oxidation to proceed extensively after each pulse, resulting in the formation of multiple isolated oxidation particles. In the absence of frequent light field modulation, these particles grow independently and interfere with one another, leading to disordered structures and the appearance of a central oxidation zone. In contrast, at high frequencies, the shorter oxidation duration limits the number of nucleation sites, while frequent modulation reinforces directional growth of emerging ridges. This supports seed-dominated stripe formation and promotes spatial coherence in the resulting LIPSSs. Overall, these observations confirm that oxidized LIPSS formation is governed by a dynamic balance between oxidation kinetics and field-guided modulation.

4. Conclusions

In this work, we systematically investigated the influence of femtosecond laser repetition frequency on the formation and morphology of oxidation-induced laser-induced periodic surface structures (LIPSSs) on amorphous silicon thin films, under a constant total pulse number. By eliminating the effects of cumulative heat buildup, we isolated the role of pulse timing and frequency in directing surface pattern evolution.

Our results reveal a clear transition from disordered central oxidation zones (COZs) to highly regular peripheral LIPSSs as the repetition frequency increases from 1 kHz to 100 kHz. The modified area decreases monotonically with frequency, while the ridge width initially increases, peaking at 10 kHz, before declining at higher frequencies; meanwhile, the LIPSS period remains nearly constant. These trends are explained by a dynamic balance between oxidation kinetics and light-field modulation frequency: low frequencies permit extensive but spatially uncontrolled oxidation, while high frequencies favor ordered growth but limit oxidation extent.

Based on experimental observations and supporting simulations, we propose that the quality of oxidized LIPSS formation is governed by the interplay between transient surface activation and repeated optical field modulation. This understanding provides valuable insight into how laser repetition frequency influences oxidation-driven nanopatterning, enabling more informed optimization of ultrafast laser parameters for applications in photonics, sensing, and surface engineering.

5. Discussion

The findings of this study provide new insight into how femtosecond laser repetition frequency can be used to control the oxidation-driven formation of LIPSSs on amorphous silicon films. Compared to prior research that emphasized heat accumulation effects in metals or crystalline semiconductors [42], our work isolates frequency as an independent tuning parameter by fixing the total pulse number and using a low-thermal-accumulation regime. This allowed us to reveal a distinct transition in pattern morphology and oxidation behavior governed by pulse timing alone. These insights refine and extend existing models such as the Optical Localization-Induced Nonlinear Competition (O-LINC) model [36] by demonstrating that repetition frequency alone can tip the balance between nucleation-dominated and field-guided growth.

In terms of practical implications, the ability to tune surface morphology solely by adjusting laser repetition frequency enables a lithography-free strategy for fabricating hierarchical nanostructures. The resulting combination of nanoparticle clusters and periodic ridges resembles biological architectures such as lotus leaves [45] and insect eyes [46],

which are widely known for their optical and wetting functionalities. By controlling ridge coherence and nanoparticle density, one may engineer surfaces with anti-reflective, polarization-sensitive, or wetting behaviors [47]. Recent work by Liu et al. [48] demonstrated femtosecond laser-induced hierarchical oxides for dual-mode visible/infrared encryption based on confined thermal aggregation. While their approach relies on localized ablation, our frequency-controlled self-organization offers a complementary pathway that may inform the future development of optical encoding, metasurfaces, and functional surfaces without the need for physical masks or multiple processing steps.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/photonics12070667/s1>.

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