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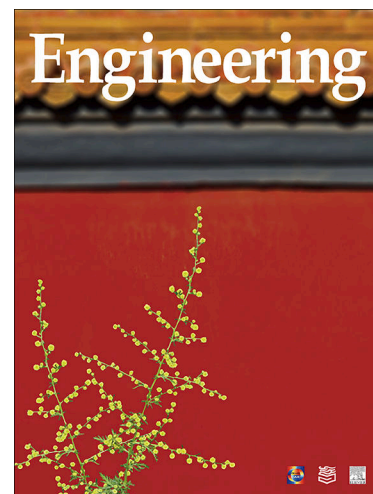
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Research

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Formation Mechanism of the Nanostructures and Crystallographic Features on Silicon Created by Ultrafast Laser Scanning

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Abstract: The manufacture of nanostructures on silicon (Si) has profound implications across diverse disciplines. Previous research has focused mainly on qualitative explanations based solely on evidence from electromagnetic and matter reorganization theories. This study designed experiments and explored the characteristics of nanostructures created by scanning with an ultrafast laser, in which experimental evidence supporting both electromagnetic and matter reorganization theories was simultaneously observed. Four distinct surface morphologies were identified, each with specific formation thresholds: 0.06, 0.09, 0.22, and 0.27 J·cm⁻². The polycrystalline Si that emerged at the apex of the monocrystalline Si matrix was directly characterized, and the occurrence of SiO₂ and α-Si was detailed. The simultaneous and distinct contributions of electromagnetic and reorganization theories were revealed. By examining the relationship between phase transitions and laser features, the conditions under which each mechanism operates were established. This study provides novel insights into the precise control of Si nanostructures, which could revolutionize applications in electronics, photonics, and materials science.

Keywords: Silicon; Ultrafast laser; Micro/nanostructures; Crystallographic features; Mechanism

1. Introduction

Notable phenomena in nature, such as colorful butterfly wings [1], hydrophobic lotus leaves [2], adhesive gecko feet [3], and drag-reducing shark scales [4], have served as sources of inspiration for scientific innovation, demonstrating that specific nanostructures on surfaces can endow materials with unique properties. The fabrication of nanostructures on the surface of silicon (Si), a cornerstone semiconductor material, has emerged as a focal point of research interest [5]. In recent years, the advent of ultrafast laser technology has introduced a novel approach to manufacturing Si with high accuracy on ultrashort timescales [6]. Its distinctive advantages [7], including high spatial resolution, minimal thermal impact, and increased efficiency and flexibility, have positioned ultrafast lasers as subjects of intense interest across a wide range of disciplines, including microelectromechanical systems [8], Si photonics [9], optoelectronic sensors [10], nanogratings [11], integrated circuits [12], biomedical engineering [13], surfaces with superwettability [14], and tribology [15]. This burgeoning interest underscores the potential of ultrafast lasers to revolutionize the fabrication of nanostructured surfaces, paving the way for the development of advanced materials and devices with tailored functions.

Extensive research has underscored the diverse applications and functions attainable through the deliberate design and control of laser-induced periodic surface structures (LIPSSs), such as particles, spikes, ripples, and holes [16 – 18]. Many studies have examined the effects of various parameters on the structural characteristics of LIPSSs. Miyagawa et al. [19] elucidated the influence of laser wavelength on the appearance of LIPSSs. Allahyari et al. [20] delineated the impact of laser fluence and repetition rate on the

features of LIPSSs. Ali et al. [21] explored the evolution mechanism of LIPSSs and quasiperiodic grooves with different pulse durations, polarization states and fluences. Zhou et al. [22] modulated the field distribution by adjusting the polarization direction and successfully fabricated regular and complex nanoparticle arrays. Kim et al. [23] introduced the influences of spot size and beam profile, achieving structural modulation of LIPSSs. Kononenko et al. [24] emphasized the influences of spot overlap, whereas Nivas et al. [25] examined the role of the incident angle of the laser beam. In addition to the modulation of LIPSSs through adjusting laser parameters, several studies have identified the ambient environment as a critical factor influencing LIPSS formation. Kudryashov et al. [26] achieved deep subwavelength, large-scale nanopatterning by immersing Si wafers in water or carbon disulfide. Wang et al. [27] reported that machining Si in deionized water facilitated oxidation inhibition. Cao et al. [28] conducted research on controlling LIPSSs on Si submerged in ethanol, and Hu et al. [29] highlighted the differences generated under vacuum and atmospheric environments. Collectively, these studies affirmed that the manifestation of LIPSS was contingent upon various parameters, including wavelength, fluence, polarization, pulse number, repetition rate, spot profile, incident angle, and the surrounding environment.

These experimental investigations into LIPSSs have been complemented by theoretical studies aimed at elucidating the mechanisms underlying their formation. As introduced by Bonse and Graf [30], the prevailing theories regarding LIPSS genesis can be classified into two categories: electromagnetic theories and matter reorganization theories. Electromagnetic theories hinge primarily on the interference phenomena between surface plasmon polaritons and the incident laser. Matter reorganization theories are predicated on the transport of laser-excited materials, driven by hydrothermal effects or the accumulation of microscopic defects, including stacking faults and dislocations. Electromagnetic theories have exhibited proficiency in elucidating the formation of LIPSSs that are typically oriented either perpendicular or parallel to the laser polarization direction and are characterized by specific periodicities. Conversely, reorganization theories play a pivotal role in explaining the LIPSSs whose orientations are not dictated by laser polarization. However, recent works have identified limitations in both electromagnetic and reorganization theories when attempting to independently interpret the formation of certain complex structures. As a result, the two theories were combined to furnish a more comprehensive explanation [31]. Nevertheless, the current explanations rely predominantly on inferences drawn from surface appearances and simulations, with direct crystallographic evidence remaining scarce [32]. In addition, existing studies have largely concentrated on the mechanisms by which various LIPSSs form under static laser irradiation, with little consideration given to the dynamic effects of scanning lasers [30]. Consequently, the formation features and mechanism of surface structures governed by ultrafast scanning lasers are not yet fully understood.

In this study, a scanning methodology was used, with adjustments to the laser power and scanning speed implemented to elucidate the transformation of morphologies and crystallographic features. Notably, the surface structures manufactured by this approach exhibited significant regularity but diverged from the specific periodicity of previously reported LIPSSs. In addition, this study yielded critical findings that served to bridge the extant gap in crystallographic evidence, providing unprecedented clarification of the concurrent manifestation and distinct contributions of electromagnetic and matter reorganization effects. The insights gleaned from this investigation substantially enrich the contemporary understanding of morphological and crystallographic transformations. These findings provide a robust theoretical framework and serve as a practical reference for the precise manufacturing of desired nanostructures and their effects on Si and other materials.

2. Materials and methods

The target material used was a monocrystalline Si wafer with a diameter of 2 inches, a surface roughness (Ra) of 0.5 nm, a thickness of 500 μm , and a crystal orientation of [100]. The experimental setup included a Huaray Pine-532-60 laser (Wuhan Huaray Precision Laser Co., Ltd., China) as the light source, delivering a maximum average power of 60 W, with a pulse duration of approximately 8 ps and a wavelength of 532 nm. The laser beam transmission system comprises several OptoSigma TFM-30C05-532 (OptoSigma Corporation, Japan) reflecting mirrors, a Jenoptik beam expander (Jenoptik AG, German), and an OptoSigma ATL-30-50PY2 (Jenoptik AG, German) focusing lens. The focusing lens, with a focal length of 49.4 mm, produced a beam diameter of 30 μm at the focal point.

The surfaces of monocrystalline Si wafers were subjected to irradiation by an ultrafast scanning laser with different laser powers and scanning speeds. The power values were obtained by adjusting the peak power percentage through the laser control system. An image of the manufacturing system is shown in Fig. 1(a). Additionally, a schematic diagram of the laser ablation process is depicted in Fig. 1(b). The trajectory of the scanning path is illustrated in Fig. 1(c); adjacent paths were spaced 500 μm apart, with both starting and ending points deliberately placed outside the Si wafer. This arrangement is designed to ensure a consistent

scanning speed within the sampling area, which has a width of 10 mm. A comprehensive list of the detailed parameters is provided in Table 1.

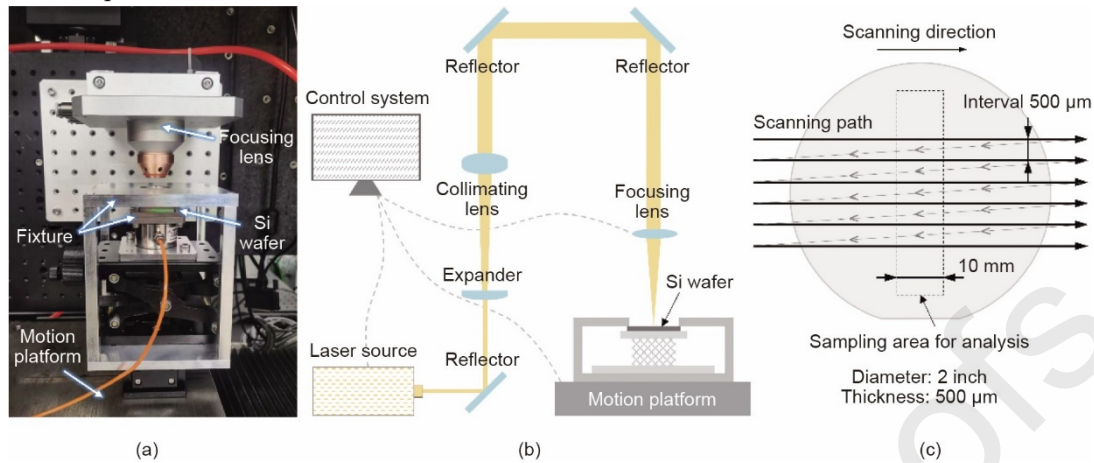


Fig. 1. Description of the experimental procedure: (a) photograph of the manufacturing system; (b) schematic diagram of the scanning ablation process utilizing an ultrafast laser; (c) scanning path and designated sampling area for subsequent analytical examination.

Table 1. Detailed parameters for the manufacturing of monocrystalline Si wafers using an ultrafast scanning laser.

Parameter	Values
Laser power (W)	0.25, 0.5, 1, 2, 3
Scanning speed ($\text{mm}\cdot\text{s}^{-1}$)	5, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200
Repetition frequency (kHz)	1000
Wavelength (nm)	532
Pulse duration (ps)	8
Defocusing amount (mm)	0
Beam diameter (μm)	30

The surface morphologies of the irradiated zones were investigated by a Tescan Clara scanning electron microscopy (SEM; Tescan Group, The Czech Republic) system. The shapes and dimensions of these zones were captured with a Zygo Nexview optical profiler (Zygo Corporation, United States). Elemental distributions were analyzed using energy dispersive spectroscopy (EDS; Tescan Group, The Czech Republic). Additionally, the phase composition and distribution were characterized by a Raman spectrometer integrated into the SEM system. To investigate the transformation mechanisms governing the surface appearance and phase distribution, an FEI Tecnai-G2-F30 TEM system (FEI Group, United States) was utilized. TEM samples were prepared using an FEI Helios NanoLab G3 FIB system (FEI Group, United States). The Transmission Kikuchi diffraction (TKD) test was conducted by a Thermo Fisher Apreo2 scanning electron microscope (Thermo Fisher Scientific Inc., United States) fitted with an Oxford symmetry electron back-scattered diffraction detector to elucidate the crystallographic features in the subsurface.

3. Results

3.1. Surface morphologies and shape features

The surface morphologies of the ablated zones at different laser powers and scanning speeds are depicted in Fig. 2(a). Within the explored range of laser parameters, the irradiated surfaces showed distinctly different morphologies. In general, four typical morphologies could be identified: morphology I, characterized by massive nanoscale granular structures; morphology II, featuring extensive wormlike structures spanning continuously from the edge to the center of the ablated zone; morphology III, consisting of numerous island structures discretely distributed within the ablated zone; and morphology IV, consisting of grooves with visible signs of fusion and solidification rather than just ablation [33]. Additionally, transitional structures exhibiting both wormlike and island features were observed during the progression from morphologies II to III. Morphologies II and III emerged as the most frequent surface structures, whereas morphologies I and IV appeared under extreme laser power and scanning speed conditions. Unlike the LIPSS created by stationary ultrafast lasers in prior studies [30,34], the surface structures produced by ultrafast scanning lasers exhibited greater complexity, marked by clear regularity and repeatability, yet lacked specific periodicity. This difference was related to variations in laser energy during the irradiation process. Specifically, for a given position, the energy imparted by the laser remained consistent when the laser beam was relatively stationary. Conversely, the energy imparted to any point on the surface varied dynamically during the scanning laser ablation process. As a result, the surface morphologies generated through the scanning ablation process differed markedly from those produced by the stationary ablation process reported previously [30,34].

The widths and depths of the ablated zones, as a function of different laser parameters, were quantitatively assessed using a Zygo profilometer, as depicted in Fig. 2(b). An increase in laser power corresponded to an increase in both the depth and width of the ablated zones. This phenomenon was attributable to the broadened range of laser energy exceeding the ablation threshold and the increased intensity of the laser–matrix interaction. A reduction in scanning speed resulted in a progressive increase in depth, whereas the width exhibited a more complex pattern of variation. The increase in depth was ascribed to the cumulative effect of the laser pulses. Notably, the width of the ablated zone remained almost unchanged when the scanning speed was adjusted between 200 and 60 $\text{mm} \cdot \text{s}^{-1}$. However, a slight reduction in width was observed at scanning speeds of 40 and 20 $\text{mm} \cdot \text{s}^{-1}$, which was postulated to be the result of the shielding effect. As the scanning speed decreased, the ablation depth and the extent of laser-induced ejection increased, which is corroborated by the increased presence of deposits at the edge of the ablated zone, as shown in Fig. 2(c). The burgeoning ejected material, which consisted mainly of plasma and vapor, disturbed the laser transmission and attenuated the energy reaching the sample surface. Consequently, the effective range of the beam energy exceeding the ablation threshold diminished, leading to a narrower ablation width. Moreover, when the scanning speed decreased to 5 $\text{mm} \cdot \text{s}^{-1}$, the width at 0.5 W further decreased because of a more intense shielding effect, whereas the width increased markedly at laser powers of 1, 2, and 3 W. This change in width was coupled with the formation of grooves, as shown in Fig. 2(c). A groove was induced when high laser power and low scanning speed were adopted, causing massive amounts of material near the groove to melt and flow to both sides under friction between the ejected material and the groove wall. As a result, the width of the ablated zone increased significantly when fusion occurred.

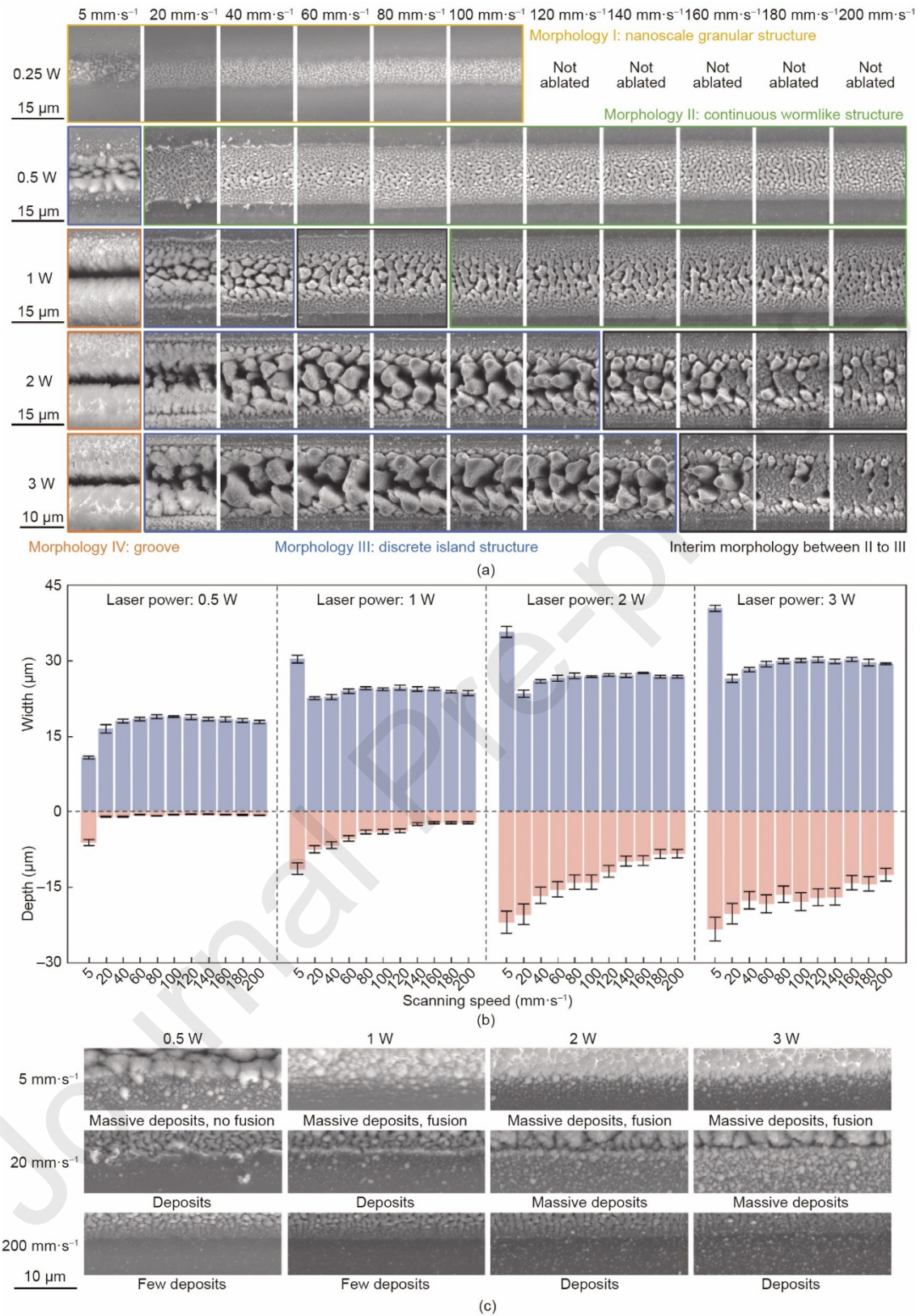


Fig. 2. Characteristics of different ablated regions at different laser powers and scanning speeds: (a) surface morphologies, with four typical morphologies identified and defined on the basis of their features; (b) shape features, showing that depth increased gradually with increasing laser power and decreasing scanning speed, whereas width increased with increasing laser power and exhibited complex variations at low scanning speeds; (c) deposition in the area adjacent the ablated zone, illustrating the extent of laser-induced ejection and its effects on ablation width.

3.2. Mechanism of various surface morphologies

The surface morphologies of the ablated regions were closely related to their depths and widths, as illustrated in Fig. 3(a). Morphological changes occurred in a regular pattern, with ablation widths ranging from less than 10 μm to more than 40 μm . Specifically, morphology I appeared when the width was less than 10 μm , whereas morphology IV emerged when the width exceeded 30 μm . The widths of morphologies II and III fell between those of morphologies I and IV, with morphology II forming when the width was between 15 and 25 μm and morphology III occurring when the width was between 20 and 30 μm . Although the ranges of widths of morphologies II and III overlapped, they could be distinguished by their depths: morphology II had a depth below 4 μm , whereas morphology III possessed a depth exceeding 6 μm . In addition, interim structures exhibiting features of both morphologies II and III possessed widths and depths between those of morphologies II and III.

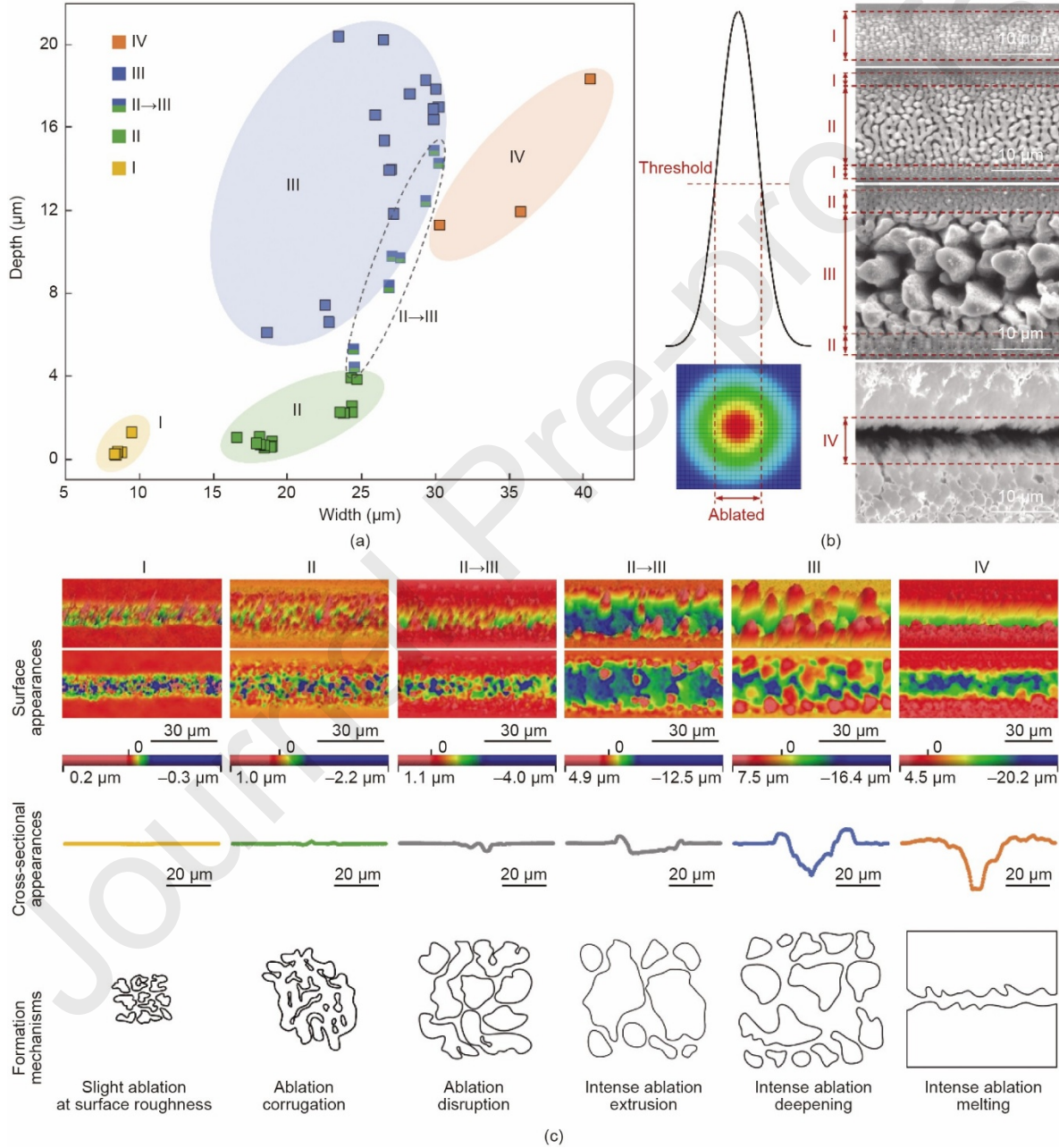


Fig. 3. Characteristics of different morphologies and mechanism by which they form: (a) relationships among the morphologies, widths and depths of the ablated regions at various laser powers and scanning speeds; (b) distribution of Gaussian laser energy and different morphologies within ablated zones under different conditions, providing a cross-check for the calculation of thresholds and ensuring the accuracy and reliability of the thresholds across different experimental conditions; (c) association of the surface and cross-

sectional appearances of different morphologies, illustrating the mechanisms by which different morphologies form.

The formation thresholds of distinct morphologies were quantified and crosschecked on the basis of the distribution of laser energy and the ranges of different morphologies within various ablated zones produced under different conditions, as revealed in Fig. 3(b) and Table 2.

Table 2

Formation thresholds for different morphologies crosschecked by various ablated zones produced with different parameters

Laser power (W)	Speed (mm·s ⁻¹)	Width (μm)	Morphologies	Threshold (J·cm ⁻²)
0.25	20	8.74	I	0.06
0.25	100	8.21	I	0.06
0.5	200	13.84	II	0.09
1	200	22.41	II	0.09
1	80	12.01	II–III	0.21
2	200	20.96	II–III	0.21
3	200	25.21	II–III	0.21
1	40	10.58	III	0.22
2	120	20.15	III	0.23
2	20	18.17	III	0.27
3	140	24.21	III	0.23
3	20	22.51	III	0.28
1	5	4.65	IV	0.27
2	5	7.55	IV	0.50
3	5	7.81	IV	0.74

The threshold H_{thr} for the laser beam with a spatial Gaussian profile is given by:

$$H_{\text{thr}} = H_0 \exp\left(\frac{-2\omega_{\text{thr}}^2}{\omega_0^2}\right) \quad (1)$$

where ω_{thr} represents half the width of the ablated region, ω_0 is the beam waist radius, and H_0 denotes the peak fluence. In the absence of relative movement between the laser and the Si matrix, H_0 can be derived as follows:

$$H_0 = \frac{2Q}{\pi\omega_0^2} \quad (2)$$

However, in this study, various scanning speeds between the laser and the Si matrix were adopted. Under these conditions, H_0 should be derived as follows:

$$H_0 = \frac{2Q}{\pi\omega_0^2 + vt\omega_0} \quad (3)$$

$$Q = \frac{P}{f} \quad (4)$$

where Q indicates the pulse energy, v and t represent the scanning speed and pulse duration, respectively, and P and f denote the laser power and repetition frequency, respectively.

Consequently, the ablation threshold of the material was determined to be $0.06 \text{ J}\cdot\text{cm}^{-2}$ when the material was first ablated at 0.25 W and $100 \text{ mm}\cdot\text{s}^{-1}$, which also represented the formation threshold for morphology I. The formation thresholds for morphologies II and III were approximately 0.09 and $0.22 \text{ J}\cdot\text{cm}^{-2}$, respectively. Interim structures between morphologies II and III tended to be generated when the laser fluence was approximately $0.21 \text{ J}\cdot\text{cm}^{-2}$, which fell between the formation thresholds for morphologies II and III. Morphology IV appeared only when the laser fluence exceeded $0.27 \text{ J}\cdot\text{cm}^{-2}$. Hence, the formation threshold increased progressively from morphology I to morphology IV, indicating that changes in surface morphology were closely related to the laser fluence. Quantifying the formation threshold is crucial for the precise control of nanostructures through manufacturing via ultrafast laser scanning.

The surface appearances and cross-sectional profiles of different morphologies were captured and are shown in Fig. 3(c). The results were compared and analyzed to elucidate the mechanisms by which various morphologies form, which are summarized as follows:

(1) Employing a low laser power (0.25 W) led to minimal ablation occurring only at isolated points where surface relief and microdefects were present. This resulted in the emergence of morphology I, which is characterized by massive granular nanoscale structures.

(2) As the laser power increased, the ablated regions expanded significantly, and the cross-sectional profile adopted a corrugated form. This phenomenon could be explained by interactions between the surface plasmon polaritons and the incident laser coupled with capillary forces. Additionally, the high repetition frequency triggered disordered convection flow [35], leading to the formation of wormlike morphology II. The formation threshold for morphology II could also be regarded as the threshold for electromagnetic effects.

(3) At a laser power of 1 W , the ablation depth increased gradually, disrupting the continuous wormlike structure to some degree. However, owing to the relatively gentle ablation process, the morphology of the ablated region under these conditions could retain corrugated features, leading to the formation of an interim morphology.

(4) When the laser power was further increased to 2 W or even 3 W , intense ablation occurred, and the irradiated surface began to soften. Unlike corrugation, extrusion of softened materials occurs under intense laser-driven shock [36] and recoil effects [37]. The extrusion and corrugation cancel each other out, resulting in a relatively flat zone at the center of the ablated zone. Consequently, the corrugated cross-sectional shape could no longer be maintained, leading to another interim morphology between morphologies II and III.

(5) The decrease in the scanning speed increased the number of repetitive pulses irradiated at the same location. This caused more violent ablation and significant removal or softening of surface materials under the incubation effect [38]. The corrugation effect weakened, with its influence on the morphology being lost. Instead, intense ablation and extrusion occurred, deepening the center of the ablated region and forming a bulge at the edge [39], resulting in the formation of morphology III.

(6) At a reduced scanning speed of $5 \text{ mm}\cdot\text{s}^{-1}$, significant heat accumulation was caused by the extended laser-material interaction time. When the laser power reached 1 W , direct melting was observed, in contrast to the softening and extrusion phenomena [40] that were typically seen at higher speeds. A groove with a cross-sectional appearance consistent with the Gaussian distribution of laser energy formed. The molten and softened materials were driven to the edge of the ablation zone under the intense friction force of ablation-induced vapor and plasma, resulting in the formation of morphology IV.

These observations demonstrated the progressive changes in surface morphology with varying laser power

and scanning speed, highlighting the complex interplay between laser parameters and material response.

3.3. Subsurface phase transformation

The phase transformation of Si could be induced by ultrafast laser irradiation, which subsequently influenced the surface morphology and functionalities [41]. Morphology II, which retained intact phase information and remained unaffected by intense ablation, was selected as a representative to investigate the phase transformation.

Raman spectroscopy was employed to preliminarily analyze the phase composition at different locations in the subsurface, including the edge of the ablated zone, the center of the ablated zone, and the Si matrix that was irradiated but unablated. The testing locations are illustrated in Fig. 4(a), and the corresponding Raman spectra are presented in Fig. 4(b). A pronounced phase transition was observed from the Si matrix to the center of the ablated zone. In the unablated Si matrix, a strong crystalline Si peak at $\sim 520\text{ cm}^{-1}$ [42] and a weak Si–O peak at $\sim 970\text{ cm}^{-1}$ [43] were identified. At the edge of the ablated zone, an intense Si–O peak at $\sim 970\text{ cm}^{-1}$ was detected alongside the crystalline Si peaks at 520 and 300 cm^{-1} [44]. In the center of the ablated zone, in addition to the crystalline Si peak at $\sim 520\text{ cm}^{-1}$, several peaks corresponding to α -Si were observed, including those corresponding to the transverse acoustic (TA) mode at $\sim 146\text{ cm}^{-1}$ [42] and the transverse optical (TO) mode at $\sim 485\text{ cm}^{-1}$ [42]. In conclusion, crystalline Si was the dominant phase, with the amorphous phases SiO_2 and α -Si emerging at different locations within the ablated zone.

To further elucidate the phase composition and distribution, transmission electron microscopy (TEM) analysis was conducted. The focused ion beam (FIB) sampling positions ranged from the matrix to the center of the ablated zone, as illustrated in Fig. 4(c). The cross-sectional appearance of the FIB sample, shown in Fig. 4(d), exhibited an overall wavelike structure, which could be explained by electromagnetic theories [30]. The wavelike structure comprises several concave and convex regions. From the edge to the center of the ablated zone, the concave regions maintained a consistent appearance, whereas the convex region clearly differed from that of the original monocrystalline Si. To further identify these changes, the subsurface atomic features of the ablated zone were analyzed. The high-resolution TEM (HRTEM) results and the corresponding results of fast Fourier transform (FFT) and inverse FFT (IFFT) were examined at several typical locations, including the edge of the ablated zone (Fig. 4(e)), the convex region without deviation from the original monocrystalline Si (Fig. 4(f)), the convex region with notable deviations from the original monocrystalline Si (Fig. 4(g)), and the concave region (Fig. 4(h)). Element compositions at different positions, labeled positions 1 to 8 in white, were measured and are presented in Table 3.

Table 3

Atomic ratios of Si and O at different locations (positions 1–8) labeled in Fig. 4.

Position	1	2	3	4	5	6	7	8
Si	36%	98%	99%	99%	98%	99%	99%	99%
O	64%	2%	1%	1%	2%	1%	1%	1%
Phase	SiO_2 , Si	Si	Si	Si	Si	Si	Si	Si

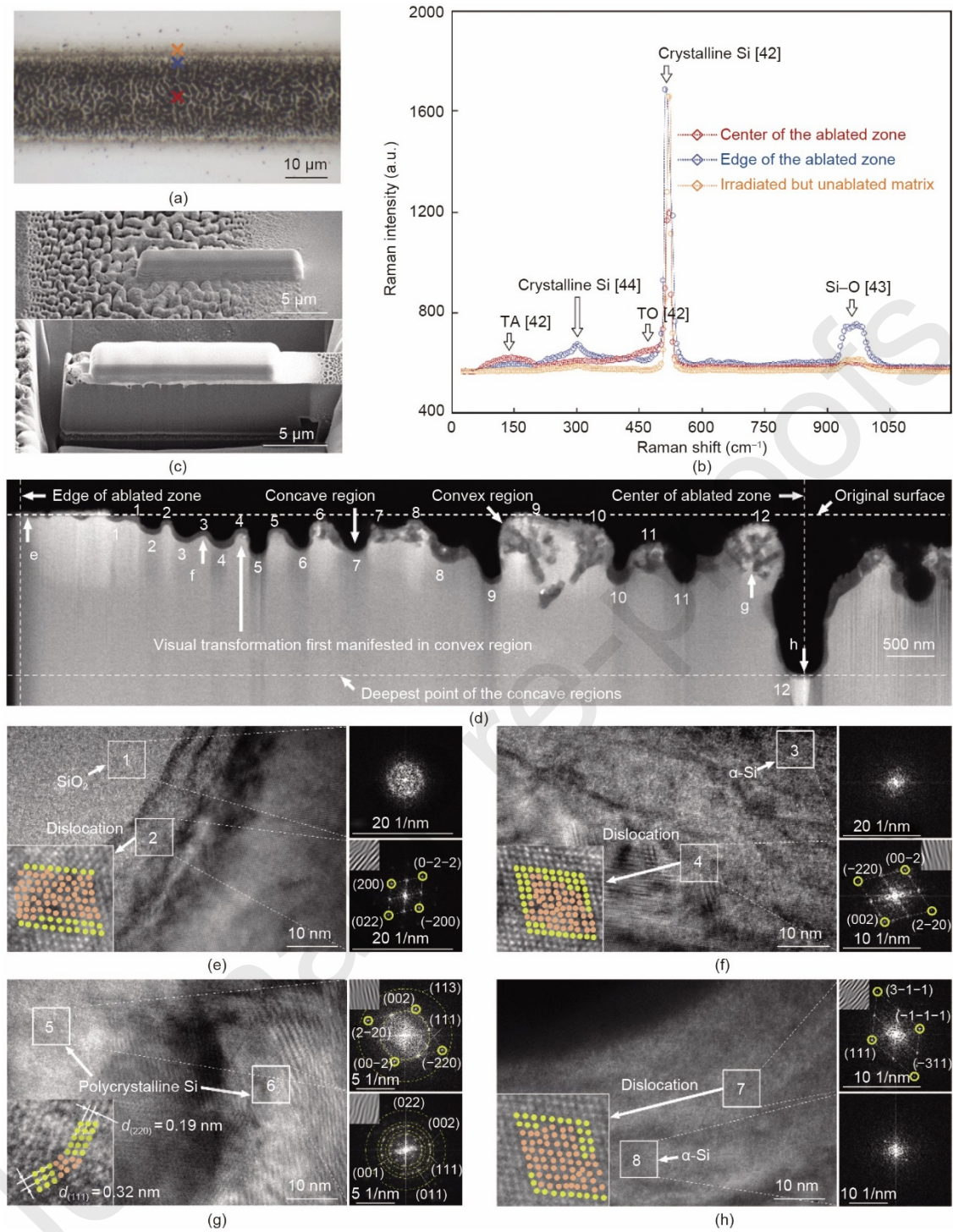


Fig. 4. Subsurface phase and atomic characteristics: (a) Raman spectroscopy testing positions, including the matrix that was irradiated but unablated (yellow mark), the edge (blue mark), and the center of the ablated zone (red mark); (b) Raman spectroscopy results, showing SiO_2 at the edge, $\alpha\text{-Si}$ at the center, and crystalline Si at both the edge and center of the ablated zone; (c) FIB sampling positions, from the Si matrix to the center of the ablated zone; (d) Cross-sectional appearance of the FIB sample, indicating the overall wavelike shape and significant transformation in the apex of convex regions; and HRTEM, FFT and IFFT results from the (e) edge of ablated zone, consisting of SiO_2 and dislocated monocrystalline Si; (f) convex region, consisting of $\alpha\text{-Si}$ and dislocated monocrystalline Si; (g) convex region, containing polycrystalline Si; and (h) concave region, consisting of $\alpha\text{-Si}$ and dislocated monocrystalline Si.

Dislocated monocrystalline Si (P2, P4, and P7) was prevalent throughout the subsurface after ablation.

These dislocations or damaged regions formed under repetitive heating and stress induced by laser pulses. Additionally, two types of amorphous phases were identified on the basis of the diffraction patterns and atomic proportions of Si and O. The first was the SiO_2 phase that emerged at the edge of the ablated zone (P1), with an irregular diffraction pattern and an atomic ratio of 9:16 (Si:O). The second was the α -Si phase found in both the convex (P3) and concave (P8) regions, characterized by irregular diffraction patterns and nearly 100% Si content. SiO_2 formed at the edge of the ablated zone, where the laser fluence was below the ablation threshold, resulting in repetitive heating rather than ablation, continuous oxidation and SiO_2 generation. The formation of α -Si was attributed to compression induced by the laser-driven shock [36] and recoil pressure [37]. Notably, polycrystalline Si phases were identified at the top of partial convex regions (P5 and P6), as demonstrated by the multiple diffraction rings shown in Fig. 4(g) and an approximately 100% Si content.

The TKD experiments were conducted to further elucidate the phase transformation (Fig. 5). The orientation maps of the convex and concave regions are shown in Figs. 5(a) and (e), respectively. The cell orientations at various locations within the convex region (P1, P2, P3, and P4) and concave region (P5, P6, P7, and P8), along with the misorientations across different lines in the convex region (L1, L2, and L3) and concave region (L4, L5, and L6), were examined, as depicted in Figs. 5(a) and (e). Pole figures (PF) and corresponding inverse pole figures (IPF) of the convex and concave regions are presented in Figs. 5(b) and (f), respectively. The orientations at different positions (P1–P8) are shown in Figs. 5(c) and (g) and Table 4, while the misorientations across different lines (L1–L6) are presented in Figs. 5(c) and (g).

Table 4

Cell orientations at different testing points labeled in Fig. 5

Location	P1	P2	P3	P4	P5	P6	P7	P8
	106.3 ◦	124.3 ◦	4.790 ◦	123.5 ◦	122.2 ◦	121.0 ◦	120.9 ◦	122.3 ◦
Orientation	39.08 ◦	25.88 ◦	44.00 ◦	27.94 ◦	27.28 ◦	27.40 ◦	27.20 ◦	27.16 ◦
n	37.06 ◦	15.98 ◦	36.02 ◦	16.22 ◦	17.53 ◦	18.38 ◦	18.73 ◦	17.43 ◦

Multiple Si grains with various orientations were observed at the apex of the convex region. The maximum misorientations from the polycrystalline Si grains to the original monocrystalline Si grain were measured at 16.05° , 15.03° , and 43.88° across L1, L2, and L3, respectively. Additionally, the α -Si phase was identified at the grain boundaries of polycrystalline Si. The recrystallization texture at the top of the convex region was characterized by TKD for the first time, which indicated the occurrence of nanoscale fusion–solidification processes in this area. In contrast, the concave regions were composed mainly of monocrystalline Si, with a minor amount of the α -Si phase present at the center of the concave surfaces, which was consistent with the TEM results.

The kernel average misorientation (KAM) maps of the convex and concave regions were measured to further analyze the distribution of laser-induced strain and distortion, which contributed to the formation of α -Si and dislocations, as shown in Figs. 5(d) and (h). In the convex region, stress concentration and distortion are predominantly observed at the grain boundary, resulting from intergranular compression induced by ultrafast laser shock and nanoscale fusion–solidification processes [45]. In contrast, in the concave region, stress concentration and distortion primarily emanated from the surface center, which was attributed to the intense recoil effect at the Gaussian distributed center of the laser.

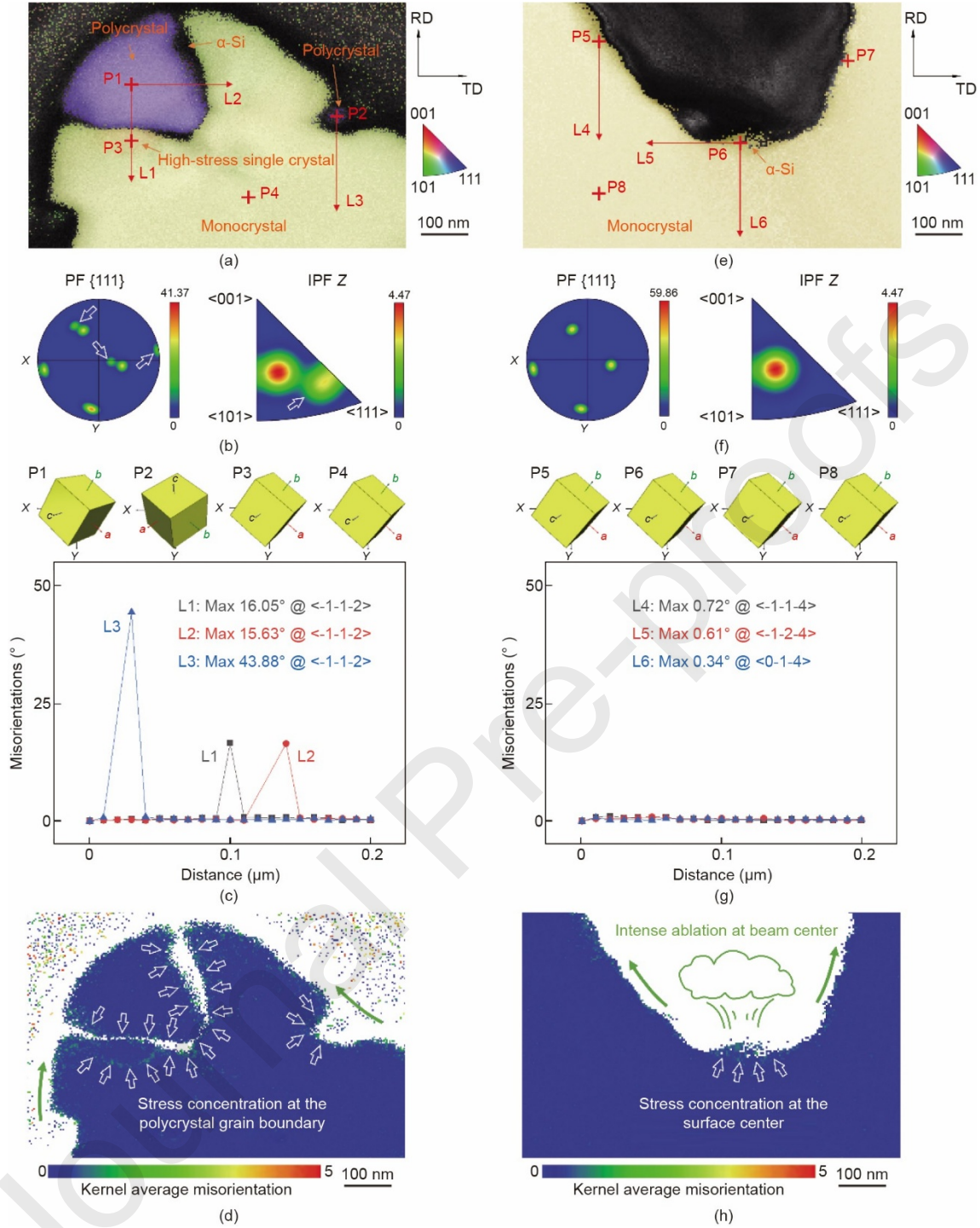


Fig. 5. TKD results: (a) Orientation map of the convex region with unresolved α -Si identified at grain boundaries, indicating test points of cell orientations (P1 and P2 in polycrystalline Si grains, P3 in high-stress monocrystalline Si grains, and P4 in the original monocrystalline Si grains) and test lines of misorientations (L1, L2, and L3); RD: rolling direction; TD: transverse direction; (b) pole and inverse pole figures of the convex region, with the orientations differing from those of the original monocrystalline Si indicated by arrows; IPF z represents the projection of the IPF graph in the z-direction. XYZ means the specimen coordinate system. *abc* means the crystal coordinate system. (c) cell orientations of P1, P2, P3, and P4 and misorientations across L1, L2, and L3; (d) KAM map of the convex region, showing high-stress areas at grain boundaries of polycrystalline Si; (e) orientation map of the concave region with little α -Si identified at the center of the subsurface, indicating test positions of the cell orientations (P5, P6, P7, and P8 in the subsurface) and test lines of misorientations (L4, L5, and L6); (f) pole and inverse pole figures of the concave region, consistent with the original monocrystalline Si grain; (g) cell orientations of P5, P6, P7, and

P8 and misorientations across L4, L5, and L6; and (h) KAM map of the concave region, indicating high-stress areas at the ablated surface, particularly at the center.

In summary, the TKD test not only validated the conclusions derived from the TEM test but also provided insights into the distribution and transformation mechanisms of subsurface dislocations and phases, including polycrystalline Si and amorphous α -Si, which differed from those of the original monocrystalline Si.

4. Discussion

One of the two existing theories, namely, electromagnetic theory and matter reorganization theory, is widely recognized for explaining structures manufactured by ultrafast lasers [46]. However, in this study, we presented crystallographic evidence demonstrating the simultaneous presence of electromagnetic and matter reorganization effects, which could not be adequately explained by either theory alone. Hence, in this study, the two theories were combined, and their roles were discussed separately. For ultrafast laser manufacturing, the interference between the laser and the surface electromagnetic wave led to a wave-like energy distribution on the surface, which diminished on both sides [30], as shown in Fig. 6(a). Material removal was driven predominantly by electromagnetic effects. In areas exposed to high interferential energy, concave regions formed because of intensified ablation, where modified surface materials were rapidly removed under the intense recoil effect of repetitive pulses [37], preventing matter reorganization. Conversely, in areas subjected to low interferential energy, convex regions formed because of mild ablation, where the modified materials remained on the surface, facilitating matter reorganization, including fusion–solidification, extrusion, and oxidation.

To further elucidate the roles played by the two theories, a schematic diagram illustrating the cross-sectional appearance of the ablated zone is presented in Fig. 6(b). Detailed analyses were conducted on the variations in the depth of the concave regions and the height of the convex regions. The height of the convex regions was measured from the deepest point of the concave regions to the unablated surface, encompassing the heights of the original monocrystalline Si and the polycrystalline Si areas. The measurement positions within the convex and concave regions are marked with white numbers from 1 to 12 in Fig. 4(d), and the corresponding results are displayed in Fig. 6(c).

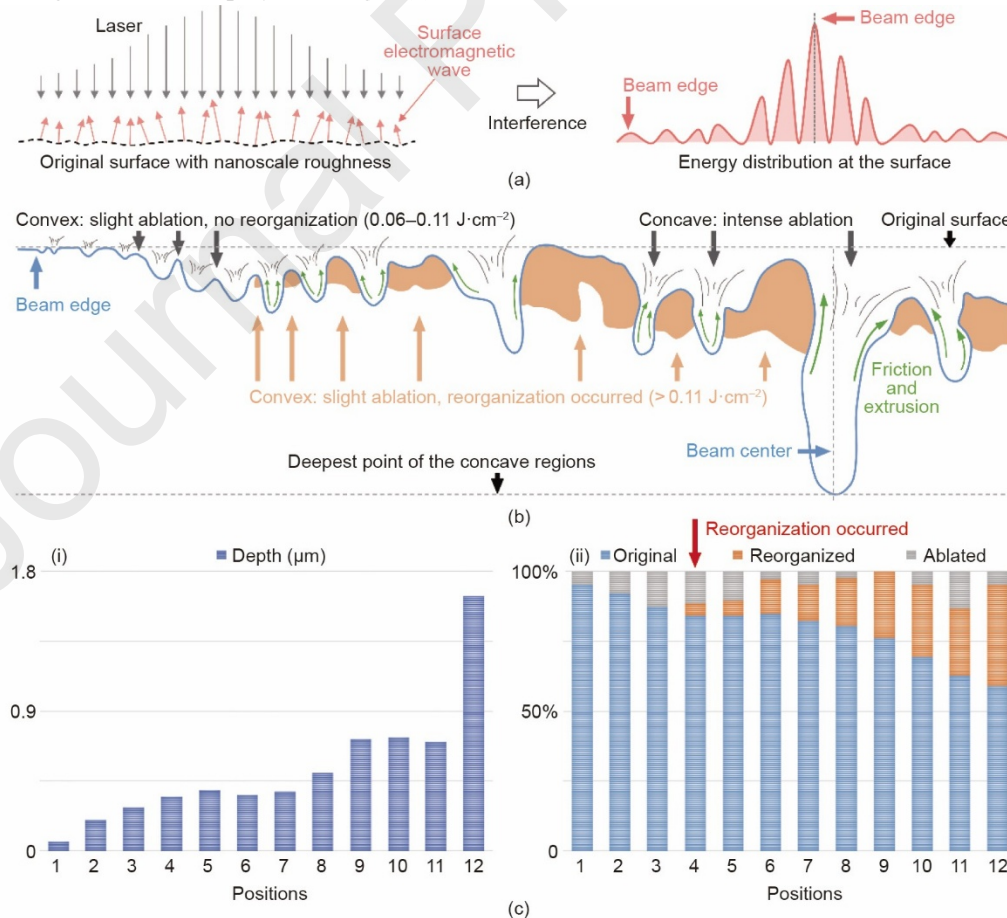


Fig. 6. Clarification of the roles played by electromagnetic and matter reorganization effects: (a) interference of the incident laser and electromagnetic waves at the surface with nanoscale roughness; (b) schematic diagram of the cross-sectional appearance and formation positions of matter reorganization, illustrating the degree of ablation induced by electromagnetic effects, and the distribution of polycrystalline Si formed under matter reorganization effects; and (c-i) depth of the concave region and (c-ii) height profile of the convex region, illustrating the influences of electromagnetic and matter reorganization effects on the shape of the ablated zone.

Owing to the Gaussian distribution of laser energy, the ablation intensity increased from the edge to the center of the laser beam. Consequently, the depth of the concave region increased, whereas the height of the original monocrystalline Si area in the convex region decreased. However, the formation and expansion of polycrystalline Si areas at the top of the convex region prevented the overall height of the convex region from decreasing. The threshold for polycrystalline transformation, a critical matter reorganization phenomenon, was determined to be $0.11 \text{ J}\cdot\text{cm}^{-2}$ on the basis of the first occurrence of polycrystalline transformation in the No. 4 convex region. This threshold was higher than both the ablation threshold for monocrystalline Si and the threshold for electromagnetic effects, indicating that while various degrees of ablation occurred throughout the ablated zone, polycrystalline transformation was restricted to specific areas. Both the electromagnetic effect and matter reorganization phenomenon coexisted at specific laser fluence levels; the electromagnetic effect existed extensively and determined the overall wavelike shape of the ablated surface, whereas matter reorganization occurred conditionally and governed the phase transformation at the apex of the convex region and influenced the final appearance.

This research elucidated the mechanism by which the surface morphology and subsurface phase formed in Si nanostructures processed by ultrafast lasers. It quantified the conditions needed for their formation and provided crystallographic evidence for the simultaneous presence of electromagnetic theory and matter reorganization theory, laying a theoretical foundation and engineering insights for the precise control of the morphology and function of Si nanostructures fabricated by ultrafast lasers.

5. Conclusions

In this study, the surface morphology and subsurface phase transformation of monocrystalline Si ablated by an ultrafast laser were investigated. Several novel findings were obtained, including the formation thresholds for typical surface morphologies, the characteristics of polycrystals, and the clarification of electromagnetic and matter reorganization effects. These results provide a new foundation for the precise control of micro/nanostructures created by ultrafast lasers. The key findings are summarized as follows:

(1) Within the range of laser powers and scanning speeds, four distinct morphologies could be identified: a nanoscale granular structure (I), a continuous wormlike structure (II), a discontinuous island structure (III), and a groove (IV). Morphologies II and III predominated, whereas morphologies I and IV formed only at extreme laser powers or scanning speeds.

(2) The threshold increased nonlinearly from 0.06 (morphology I) to $0.27 \text{ J}\cdot\text{cm}^{-2}$ (morphology IV), reflecting fundamentally different material response regimes: surface-dominated electromagnetic effects (I and II) versus bulk matter reorganization requiring viscous flow and phase change (III and IV). This distinction arose because morphology I/II involved surface modification (ablation/corrugation), whereas morphology III/IV required overcoming higher energy barriers for extrusion and melting.

(3) SiO_2 emerged at the ablation edge as a result of continuous oxidation, facilitated by the incubation effect of laser heat. Polycrystalline Si emerged in the convex region through nanoscale fusion–solidification processes. α -Si developed at the center of the concave surface and at the grain boundaries of polycrystalline Si under various types of compression.

(4) The electromagnetic effects dictated material removal and the overall shape of the ablated zone, whereas matter reorganization governed the polycrystalline transformation and modified the final appearance of the surface structure. The threshold for matter reorganization was calculated to be $0.11 \text{ J}\cdot\text{cm}^{-2}$, which was higher than the threshold for electromagnetic effects ($0.09 \text{ J}\cdot\text{cm}^{-2}$).

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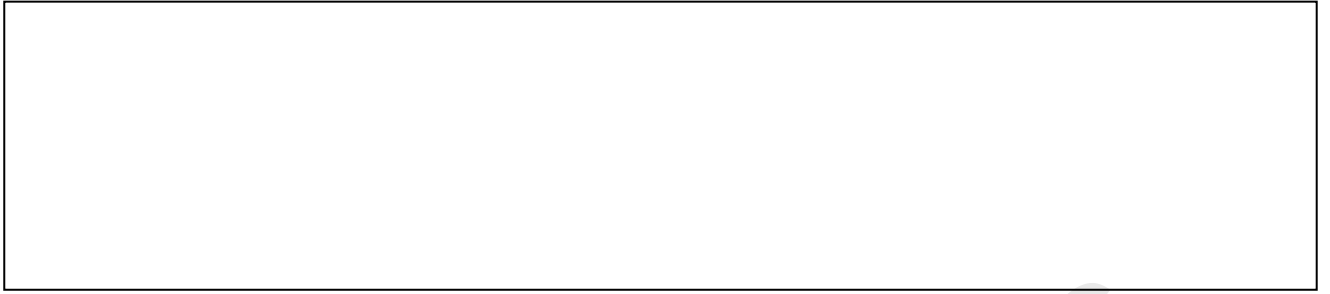
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