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Abstract. Nanoripples and nanoparticles have been fabricated on the surface of a silicon carbide sample with the irradiation of an 800-nm femtosecond laser in an underwater environment. When a linearly polarized laser was used, the nanoripples were perpendicular to the polarization direction of the incident laser, and the period of the nanoripples was dependent on the number of pulses. When a circularly polarized laser was used, nanoparticles with a diameter of approximately 80 nm were formed. In addition, we observed two kinds of nanoripples on the sidewall of the silicon carbide microgroove fabricated by femtosecond laser irradiation followed by chemical wet etching. When the polarization direction was aligned perpendicular to the writing direction, ripples parallel to the surface of the sample were formed. We attribute the formation of this kind of ripple to interference of the incident laser and the reflected wave. When the polarization direction was aligned parallel to the writing direction, the ripples are perpendicular to the surface of the sample. We attribute the formation of this kind of ripple to interference of incident laser and bulk electron plasma wave. A scanning electron microscope equipped with an energy dispersive X-ray spectroscope was employed to characterize the morphology of the structures.
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Keywords: nanoripples; nanoparticles; femtosecond laser; silicon carbide.

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1 Introduction

Surface patterning of two-dimensional nanostructures has become increasingly important for applications in electronics, quantum electronics, optoelectronics, tribology, nanoelectromechanical-systems, high-density optical storage, and light emitting diodes.[1,2] For example, Deki et al.[3] reported the enhancement of local conductivity in silicon carbide (SiC) with nanoripples. Zhao et al.[4] found a great improvement of photocurrent for photovoltaic devices application originated from the formation of nanostructures on the surface of the SiC sample. Silicon-based devices have been well-developed. Unfortunately, the devices are generally limited in electronic devices performance to below 250°C and in mechanical devices performance to below 600°C.[5] They are not suitable to work in a corrosive environment because Si could be easily etched by an acid solution. SiC is a promising candidate for optoelectronic devices because it is a wide-bandgap material. SiC-based devices are capable of working in harsh temperatures, wear, chemical, and radiated environments.[6,7]

Recently, the ultrafast laser has proved to be a versatile tool for micromachining.[8,9] Especially, it has proved as an effective tool for surface patterning micro- and nanostructures for SiC. Laser patterning has several prominent advantages over conventional methods, namely noncontact processing, fast removal rates, and simple technological processing. Additionally, laser direct writing is capable of fabricating three-dimensional devices due to the fact that the sample can be mounted onto a programmable positioning stage. Accordingly, surface patterning of micro- and nanostructures in SiC using femtosecond lasers has been extensively investigated.[10–14]

However, femtosecond laser patterning nanostructures in SiC suffers from several limitations. First, since these experiments were performed in ambient air, the chemical compositions of the induced grooves would not be pure silicon and carbon anymore. This means foreign species such as oxygen (O) would contaminate the structures, which has a bad effect in terms of the integration of SiC-based devices. Second, during the laser treatment process, the light is scattered by the debris redeposited on the surface, reducing the laser energy on the incident spots, hence decreasing the depth of the nanogrooves.

Under-water micromachining has drawn increasing attention from researchers because of its advantages, such as higher-plasma pressure due to confinement, more effective cooling of workpiece and ejected material, and smaller focal spot size. There have been many publications on the micro- and nanomachining underwater environment.[15,16] It is expected that clear nanostructures pattern could be achieved since the laser irradiation is conducted underwater. However, there has been no report on using this method to fabricate nanostructures in SiC.

In this work, we proposed methods for fabrications of nanostructures on SiC surface and on the sidewalls of SiC microgrooves, in which the contamination of O was reduced. First, the nanoripples were fabricated on the surface of SiC sample by an irradiation of an 800-nm femtosecond laser in

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an underwater environment, in which the influence of laser scanning velocity on the period of the nanoripples was investigated and the role of water during the irradiation was discussed. Second, the nanoripples on the sidewalls of the microgrooves were fabricated using laser irradiation and chemical etching. Laser induced structural change (LISC) zones were produced with the irradiation of an 800-nm femtosecond laser. Then, acid solution was used to remove the LISC zones, forming a groove with clear nanoripples on its sidewalls. We discuss the possible formation mechanism of the ripples.

2 Experimental Setup

Figure 1 shows the schematic experimental setup for using laser irradiation to fabricate nanostructures on/in SiC. The experimental setup consists of a femtosecond laser source, an attenuator, a neutral density filter, a mechanical shutter, a *xyz* movable stage, a computer, and a CCD camera. The light source used was an amplified Ti: sapphire femtosecond laser system (Coherent Inc.,) with a pulse duration of 150 fs, wavelength of 800 nm, and repetition rate of 1 kHz. The attenuator provided a convenient way to adjust the laser energy and the mechanical shutter was employed to control the access of laser beam. The movable stage, on which the SiC sample could be mounted, was controlled by the computer program, and allowed us to fabricate structures on the sample with a high precision. The CCD camera was connected to a computer for clear online observation of the SiC sample surface during fabrication.

In our experiments, a 6H-SiC sample with 350 μm in thickness was used. The sample was cleaned in acetone and deionized water with an ultrasonic field for 10 min each before being mounted on the movable stage. The laser beam was focused onto the sample via a 10× microscope objective with a numerical aperture of 0.3. The focal length of microscope is 16.5 mm. The radius of the spot at the sample surface is about 8.7 μm. The beam profile at the focal point is nearly a Gaussian distribution with a circular shape. During fabrication, the surface of the SiC sample could be seen either via optical microscope or on the computer screen connected to CCD camera. A scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscope (EDS) was employed to characterize the morphology and chemical composition of the nanostructures. The periods of the nanostructures were estimated from SEM pictures. For each experiment, we collected 10 areas and measured the period of the nanostructure in each one. Finally, the average result of ten areas was the period of the nanostructure.

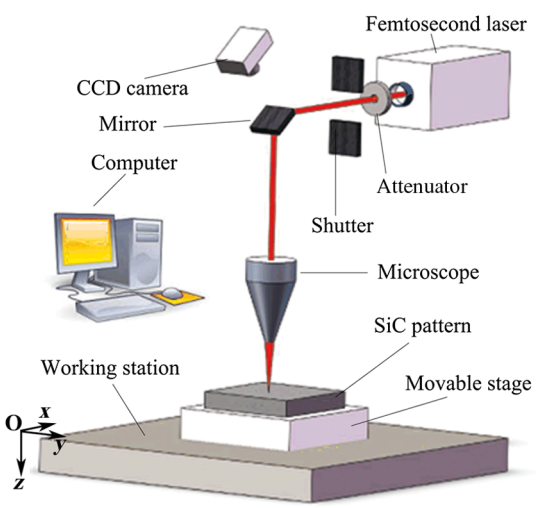

Fig. 1 Experimental setup of using laser irradiation to fabricate micro- and nanostructures on/in SiC using a femtosecond laser.

3 Experimental Results and Discussion

Figure 2 shows the evolution of nanostructures on SiC surface fabricated with an 800-nm femtosecond laser at different number of pulse. The sample was immersed in water liquid; the height of the water column is 1000 μm from the surface of the pattern. The scanning direction was parallel to the *y* axis, which was parallel to the polarization direction of the incident laser. The pulse energy was fixed at 30 μJ. In consideration of the Fresnel refraction at interfaces, the laser fluence was estimated to be 20.2 J cm^{-2}, whereas the number of pulses was varied from to 5 to 85. Note that the size of area in which the ripples are formed is dependent on the laser fluence. At low-laser fluence, the size of the ripples area increases with the increase of laser fluence. At high-laser fluence, a deep hole is formed at the center, and the ripples can only be formed at the periphery. In our experiments, the radius of the ripples area was about 5 μm. After irradiation, the sample was cleaned in acetone and deionized water for 10 min each.

As the number of pulse was increased, the nanostructures on the surface grew as follows: random structure on surface, coarse ripples (nanoripples with period of 450 nm), and fine ripples (nanoripples with period of 150 nm). The ripple was perpendicular to the laser polarization direction. In Fig. 2(a), as the number of pulse was 5, the periodic structure could not be formed. As the number of pulse increased to 7, nanoripples with the period of about 450 nm (coarse ripples) came to being, however, the feature was not very clear as shown in Fig. 2(b); as the number of pulse was 9, coarse ripples were formed and could be seen clearly as shown in Fig. 2(c). Figures 2(d) and 2(e) show the ripples fabricated with the number of pulse of 12 and 17. And as the number of pulse was larger than 17, nanoripples with period much smaller than wavelength were formed as shown in Figs. 2(f) and 2(g). It should be noticed that when irradiated in air the ripples were not obvious as shown in Figs. 2(h) and 2(i). It is obvious that the number of pulse was the decisive factor that influences the formation of the nanostructure on the surface of SiC. This is due to the pulse accumulating effect. As the number of pulse increases, the laser energy accumulated on the unit area of the SiC sample increases and the ablation threshold decreases. The result reported here is similar to the phenomenon of laser-induced nanoripples on silicon surface immersed in water in Ref. 17, and can be attributed to the excitation of surface plasmon polaritons (SPPs) in the surface layer. Because of irradiation with an 800-nm laser in ambient air, the ripples were hard to observe as shown in Figs. 2(h) and 2(i). This is maybe because when irradiated in ambient air, the debris redeposited on the surface during the laser treatment could scatter the incident light, damaging the structure of the nanopatterns on the surface.

EDS results as shown in the insets of Figs. 2(e) and 2(h) show the chemical compositions of the nanoripples

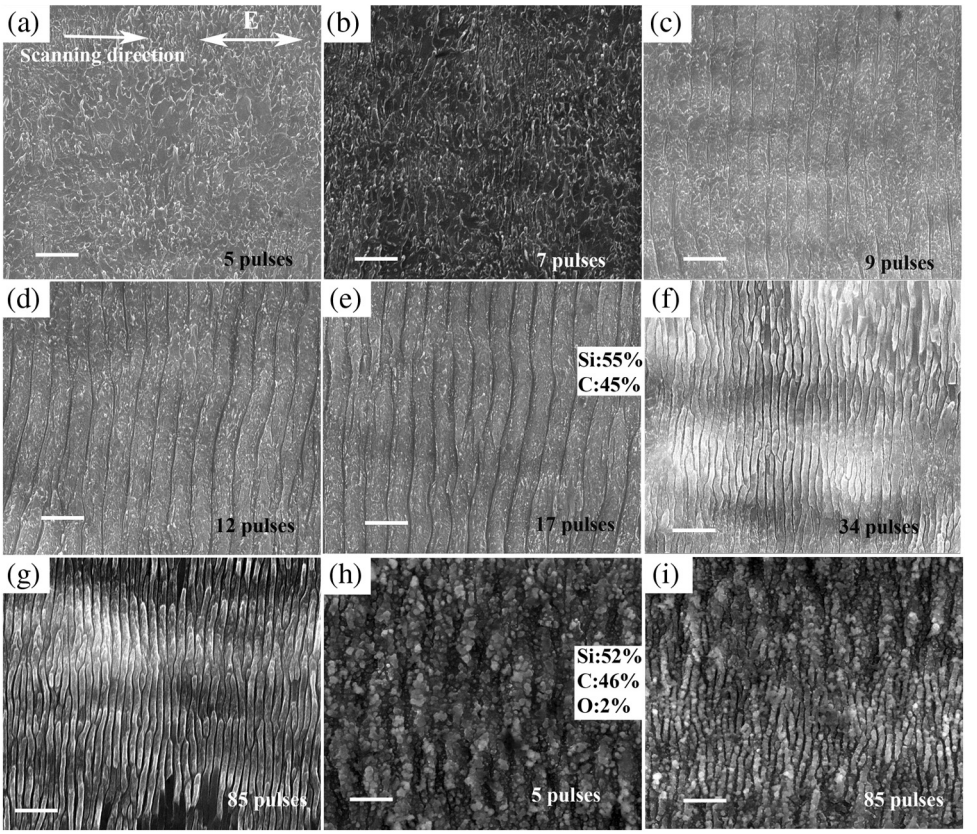

Fig. 2 Evolution of nanoripples on SiC surface when irradiated with an 800-nm femtosecond laser underwater: (a) 5 pulses, the inset arrows shows the polarization direction; (b) 7 pulses; (c) 9 pulse; (d) 12 pulses, (e) 17 pulses, the inset shows the elements percentage on the area; (f) 34 pulses; (g) 85 pulses; representative morphology of surface when irradiated in air at different scanning velocity (h) 5 pulses, the inset shows the elements percentage on the area; (i) 85 pulses. The scale bar is 1 μm. The scanning direction is parallel to the polarization direction.

fabricated in an underwater environment and in ambient air, respectively. It could be seen that the ratio of Si and C was changed after the irradiation underwater. However, O was not found on the surfaces. For the surface irradiated in ambient air, in addition to the change in the ratio of Si and C, O was incorporated into the material. We explain this result as follows. For ultrashort laser pulses, multiphoton absorption is considerably strong. Although 800-nm photons cannot meet the 6H-SiC band gap energy (3.1 eV) requirements, bond breaking is induced by multiphoton absorption associated with the extreme intensity. As a result, dangling bonds appeared in the crystal lattice of SiC. The incorporation of O in the material when irradiated in air could be attributed to the trapping effect of the dangling bond.[18,13] In contrast, when irradiated under water, O from the air was isolated by the water. This means that the method could be used to eliminate the contamination of O in to the surface of the sample.

We also study the nanostructures generated by circularly polarized light. The laser was adjusted to be circularly polarized light using a quarter-wave plate. Figure 3 shows the morphologies of the nanostructures on SiC fabricated with a circularly polarized 800-nm femtosecond laser. The pulses energy was 20 μJ corresponding to a laser fluence of 14 J cm^{-2}. As shown in Figs. 3(a) and 3(b), as the number of pulse was 12, the nanoriple with period of 150 nm was

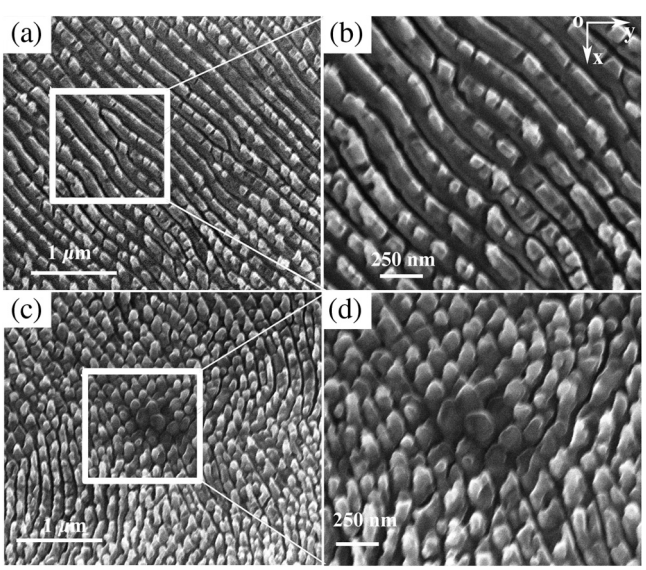

Fig. 3 Scanning electron microscope (SEM) images morphology of nanoparticles on surface of SiC irradiated with circularly polarized light: (a) 12 pulses; (b) magnified view of area marked with rectangle in (a); (c) 34 pulses; (d) magnified view of area marked with rectangle in (c).

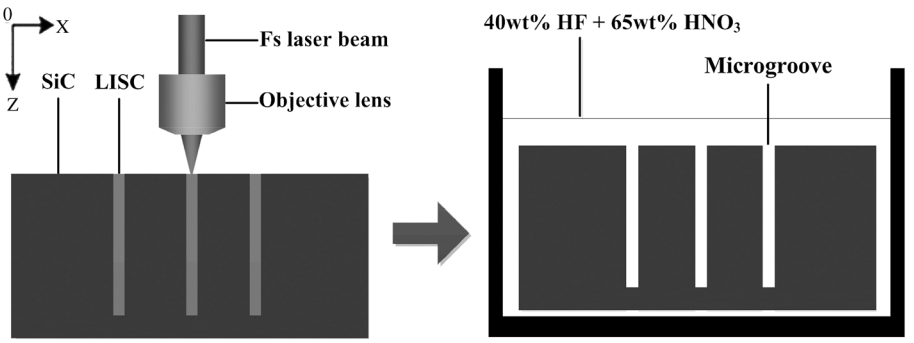

Fig. 4 The schematic diagram of fabricating microgroove in SiC: (a) experiment setup for laser irradiation; (b) experiment setup for chemical etching.

formed on the surface of the sample; the ripples are 45 deg in the vertical direction. As the number of pulse was 34 pulses, the particles were formed as shown in Figs. 3(c) and 3(d). The size of the particles is about 80 nm and the period is about 150 nm. The nanoparticles formation is attributed to the second harmonic generation (SHG) of the incident laser.[19] The periodicity of the particle is calculated by $\lambda/(2\times n)$.[19] λ (800 nm) is wavelength of incident wave, and n (2.7) is the refractive index of SiC.

Figure 4 shows the technological process for fabricating microgrooves in SiC. First, the LISC zones are produced with irradiation of an 800-nm femtosecond laser as shown in Fig. 4(a). Then, mixed solution of HF and HNO_3 is used to remove the LISC zones, forming the grooves in SiC as shown in Fig. 4(b). In order to exam the nanostructures on the sidewall of the microgroove, the sample was cut at the position of the center of the groove. A SEM equipped with an EDS was employed to analyze the morphology and chemical compositions of the nanostructure on the sidewall of the SiC grooves, respectively.

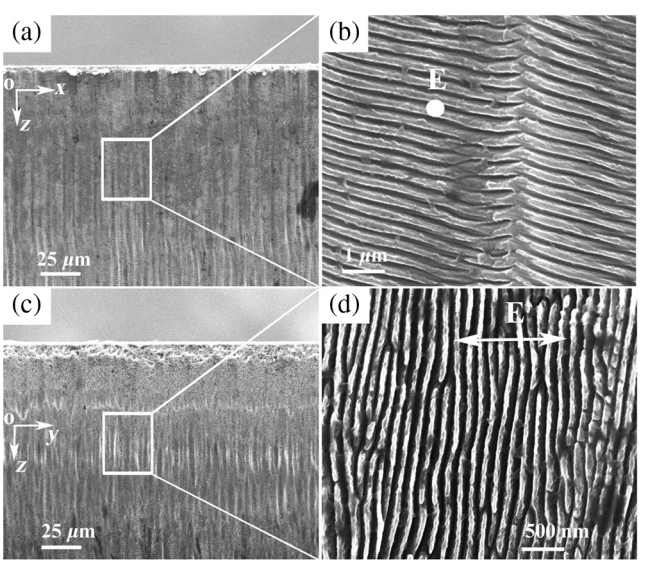

Fig. 5 SEM images of the nanoripples on the sidewall of SiC microgrooves: (a) sidewall of the groove with the the ripples parallel to the groove direction; (b) magnified view of the ripples; the inset shows the polarization direction E; (c) sidewall of the groove with the ripples perpendicular to the groove direction; (d) magnified view of the ripples; the inset shows the polarization direction E.

Figure 5 shows the nanoripples on the sidewall of the SiC microgrooves fabricated using a femtosecond laser irradiation and chemical selective etching with mixed solution of HF and HNO_3. The grooves were fabricated in ambient air. The pulse energy and the number of pulses were 30 μJ and 3000, respectively. The laser fluence was estimated to be 18.1 J cm^{-2}. The formation of SiC grooves is attributed to the chemical reactions of the LISC with a mixed solution of HF and HNO_3.[13] As the polarization of laser is aligned perpendicular to the writing direction, the period of the ripples is about 400 nm, and it aligned parallel to the surface of the sample as shown in Figs. 5(a) and 5(b). When the polarization of the laser is aligned parallel to the writing direction, the ripples perpendicular to the groove direction with periodicity of 150 nm were formed. Figures 5(c) and 5(d) show the morphology of the ripples aligned perpendicular to the surface of the sample.

The ripples in Fig. 5(b) could be attributed to the standing wave generated in z direction due to the interference between the incident wave and the reflected wave from the interface of laser affected zone and the pristine material which was perpendicular to the z direction.[10] The formation of the standing wave led to the permanent structural changes in SiC, forming the preform of the nanoripples. As the sample was treated with proper etching technique, the laser affected zone was removed, resulting in the nanoripples on the sidewalls of the grooves. The formation of the ripples in Figs. 5(c) and 5(d) is attributed to the interference of the incident laser field electric field of the bulk electron plasma wave, resulting in periodic modulation of the electron plasma concentration and permanent structural changes in SiC at the edge of the LAZ.[20] Furthermore, it was confirmed that the chemical compositions of the nanostructure were Si and C.[13] This means that the method can be used to remove the contamination from in the structure. This is very beneficial for device integration and bio-compatibility.

4 Conclusions

In conclusion, we fabricated several kinds of nanostructures including coarse nanoripples, fine nanoripples, and nanoparticles on SiC surfaces, and nanoripples on the sidewalls of a microgroove. The morphology and chemical compositions of the ripples were analyzed by SEM equipped with an EDS. When irradiated with linearly polarized light, with the increase in the pulse number, the nanostructures on the surface successively evolved as follows: the random structure,

the coarse ripple with period close to the wavelength, and fine ripple with a period much smaller than the wavelength. The evolution of the ripples can be explained considering the excitation of SPPs in the surface layer. When irradiated with circularly polarized light, nanoparticles with period of 150 nm and diameter of 80 nm were formed. The formation of nanoparticle is attributed to the SHG. In addition, the nanoripples on the sidewall of microgroove were fabricated. As the polarization of the laser was aligned perpendicular to the writing direction, ripples parallel to the surface of the sample were formed. We attribute the formation of this kind of ripple to the interference of the incident laser and the reflected wave. When the polarization of the laser was aligned parallel to the writing direction, the ripples perpendicular to the surface of the sample were formed. We attribute the formation of this kind of ripple to the interference of the incident laser and bulk electron plasma wave. The nanostructures fabricated here may have potential applications in photovoltaic field and microfluidic devices.

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References

1. K. Zhou et al., "Fabrication of complex nanostructures on ZnO crystals by the interference of three femtosecond laser beams," *Opt. Laser. Eng.* **50**(2), 297–302 (2012).
2. R. Buividas et al., "Ripple-patterned substrates for light enhancement applications," in *Proc. SPIE* **7376**, 737602 (2010).
3. M. Deki et al., "Enhancement of local electrical conductivities in SiC by femtosecond laser modification," *Appl. Phys. Lett.* **98**(13), 133104 (2011).
4. Q. Z. Zhao et al., "Enhancement of optical absorption and photocurrent of 6H-SiC by laser surface nanostructuring," *J. Appl. Phys. Lett.* **91**(12), 121107 (2007).
5. M. Mehregany et al., "Silicon carbide MEMS for harsh environments," *Proc. IEEE* **86**, 1594–1609 (1998).
6. I. Shigematsu et al., "Analysis of constituents generated with laser machining of Si_3N_4 and SiC," *J. Mater. Sci. Lett.* **17**(9), 737–739 (1998).
7. B. Pecholt, S. Gupta, and P. Molian, "Review of laser microscale processing of silicon carbide," *J. Laser Appl.* **23**(1), 012008 (2011).
8. L. Cerami et al., "Femtosecond laser micromachining," in *Ultrafast Nonlinear Optics*, pp. 287–321, Springer International Publishing, Switzerland (2013).
9. N. H. Rizvi, "Femtosecond laser micromachining: current status and applications," *Riken Rev.* 107–112 (2003).
10. V. Khuat et al., "Uniform nano-ripples on the sidewall of silicon carbide micro-hole fabricated by femtosecond laser irradiation and acid etching," *Appl. Phys. Lett.* **104**(24), 241907 (2014).
11. S. H. Kim, I. B. Sohn, and S. Jeong, "Fabrication of uniform nanogrooves on 6H-SiC by femtosecond laser ablation," *Appl. Phys. A* **102**(1), 55–59 (2011).
12. X. J. Wu et al., "Formation mechanisms of uniform arrays of periodic nanoparticles and nanoripples on 6H-SiC crystal surface induced by femtosecond laser ablation," *Appl. Phys. A* **86**(4), 491–495 (2007).
13. K. Vanthanh et al., "Fabrication of micro-grooves in silicon carbide using femtosecond laser irradiation and acid etching," *Chin. Phys. Lett.* **31**(3), 037901 (2014).
14. L. Gemini et al., "Periodic nanostructures self-formed on silicon and silicon carbide by femtosecond laser irradiation," *Appl. Phys. A* **117**(1), 49–54 (2014).
15. M. Y. Shen et al., "Femtosecond laser-induced formation of submicrometer spikes on silicon in water," *Appl. Phys. Lett.* **85**(23), 5694–5696 (2004).
16. V. Khuat et al., "Deep-subwavelength nanohole arrays embedded in nanoripples fabricated by femtosecond laser irradiation," *Opt. Lett.* **40**(2), 209–212 (2015).
17. G. Miyaji et al., "Mechanism of femtosecond-laser-induced periodic nanostructure formation on crystalline silicon surface immersed in water," *Opt. Express* **20**(14), 14848–14856 (2012).
18. T. Kudrius, G. Šlekys, and S. Juodkazis, "Surface-texturing of sapphire by femtosecond laser pulses for photonic applications," *J. Phys. D Appl. Phys.* **43**(14), 145501 (2010).
19. T. Q. Jia et al., "Formation of nanogratings on the surface of a ZnSe crystal irradiated by femtosecond laser pulses," *Phys. Rev. B* **72**(12), 125429 (2005).
20. R. Bhardwaj et al., "Optically produced arrays of planar nanostructures inside fused silica," *Phys. Rev. Lett.* **96**(5), 057404 (2006).

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