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# Deposition and melting behaviors for formation of micro/nano structures from nanostructures with femtosecond pulses

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This study reported the fabrication of a large area of micro/nano structures with different morphologies and sizes by the deposition of ablated material and melting of material on silicon through a line-shaped femtosecond laser beam irradiation. The evolution of micro/nano structures on the silicon surface was demonstrated with the laser fluence of 0.64 J/cm$^2$. It was found that the melting of material was responsible for the formation of the micro-protrusions from laser-induced periodic surface structures (LIPSSs). Additionally, the deposition fell on the surface of the micro-protrusions in oblique incidence way, causing LIPSSs obscure and even invisible. As a consequence, those micro-protrusions gradually evolved into the micro-spikes with the ladder-like surface. Then, various laser fluences were applied to regulate the deposition and melting behaviors of silicon, to obtain the micro/nano structures with different morphologies and sizes. The formation mechanism of these micro/nano structures was analyzed. On this basis, the optical properties test showed that best anti-reflectivity was referred to the sample full of micro-spikes with the ladder-like surface, and the average reflectance has decreased from ~38.17% of the planar silicon to~4.75% in the waveband between 300 and 1000 nm.


## 1. Introduction

Surface micro/nano structures can significantly alter the physical properties of the material, for example, anti-reflective properties [1], wetting properties [2], and other properties [3–6], thus the fabrication of surface micro/nano structures have attracted substantial attention. Laser processing, characterized of non-contact, has been widely used in formation of micro/nano structures on the surface of material [7,8]. For the conventional laser ablation methods, the micro/nano structures are fabricated by the laser drilling and grooving [9,10], where the microstructures with the feature size below 5 μm using direct laser ablation is quite difficult to obtain. The ultra-short pulsed lasers cause a relatively small thermal-transfer-induced energy redistribution [11], which has proved to be a useful technology for the creation of micro/nanostructures on different kinds of materials [12–14]. The dimensions of microstructures range from several microns to ten microns can be produced with the ultra-short pulsed lasers.

Recently, the evolution of ultrafast laser-induced micro/nano structures has been widely studied. Laser-induced periodic surface structures (LIPSSs) on the surface of the material can be produced with laser fluence close to or below the ablation threshold of the material, and the LIPSSs will gradually evolve into microstructures as the laser fluence increases [15]. A lot of research was devoted to the effect of laser parameters on the LIPSSs, and two kinds of LIPSSs, low spatial frequency LIPSSs (LSFL) and high spatial frequency LIPSSs (HSFL), have been obtained on the material surface [16–18]. Meanwhile, the formation mechanism of LIPSSs has been extensive studied in recent years. It is generally accepted that these LSFLs were generated by interaction of the incident laser beam with a surface electromagnetic wave generated on the rough surface, or excitation of surface plasmon polariton (SPP) [19,20], while these HSFL can be interpreted as self-organization [21], second harmonic generation [22], third harmonic generation [23], another kind of excitation of SPPs etc.

In the aspect of laser-induced surface microstructures, the special morphology of microstructures can be obtained by changing the laser parameters or the processing environment. Ma et al. [15] fabricated four kinds of microstructures: well-defined LIPSSs, obscured LIPSSs, micro-spikes with nano-holes, and separated

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micro-spikes via the variation of laser irradiation parameters on the silicon surface in air. Zhu et al. [24] induced the sharp conical spike array on the silicon surface under femtosecond (fs) laser irradiation in SF6 ambient. Ge et al. [25] reported that novel dual-scale structures were obtained by fs double pulse train one-step irradiating silicon in water, where the dual-scale structures consist of micro-spikes and LIPSSs. K.M.T. et al. [26] reported the bumpy structures on titanium by fs-laser irradiation. Guo from China-US Photonics Lab is famous for experimental investigation of self-organizing structures, the group of Guo produced columnar microstructures on the titanium surface [27] and array of parallel nanostructure-textured microgrooves on the silicon surface [28]. However, the disappearance of LIPSSs, and the evolution of microstructures with different morphologies and sizes under different laser parameters, has not been reported yet.

In addition, it was reported that the formation mechanism of the microstructures was attributed to a combination of capillary waves on the molten silicon surface and laser-induced etching of material [29], self-organized [30], Mie scattering phenomenon of light [31] or the modulated laser ablation [15]. In the laser machining process, the deposition of ablated material and melting of material occur on the material surface [32], and these behaviors may affect the formation of micro/nano structures. Nevertheless, there is little literature available on the influence mechanism of the deposition and melting behaviors on the micro/nano structures.

In this paper, we propose a method to regulate the deposition of ablated material and melting of material on the silicon surface with a line-shaped femtosecond laser beam pulses, to obtain a large area of micro/nano structures with different morphologies and sizes in air. The evolution of micro/nano structures on the silicon surface was demonstrated. On this basis, micro/nano structures with different morphologies and sizes were fabricated and the regulating mechanism of the deposition and melting behaviors for formation of micro/nano structures was analyzed. Finally, the optical properties of the silicon substrate with different micro/nano structures were detected.

## 2. Experimental conditions and parameters

Commercially available p-type silicon wafers (100) with a thickness of 525 μm were used here. Before laser irradiation, the silicon wafers were rinsed in an ultrasonic cleaner with acetone, ethanol, and deionized water for 8 min, respectively.

A Nd:YLF solid state femtosecond laser system (Spitfire Ace, Spectra-physics Inc.) based on pulse regenerative amplification was used. The laser system delivers 120-fs-width pulses with a maximum power of 5 W at a repetition rate of 1 kHz, and it operates at the wavelength of 800 nm. The laser beam has a Gaussian energy density distribution with a beam diameter of 12 mm (@ 1/e2). The experimental setup is depicted in Fig. 1. A diaphragm is used to shape the laser beam, and a pyroelectric detector is used to monitor the laser power in real-time in conjunction with a beam-splitter located along the primary laser path. Laser Microfabrication Workstation (Newport, USA) with a movement precision of ±750 nm, is controlled by a computer and used to precisely position the samples. The laser scanning velocity, the scanning length could be set via the software. The laser beam was focused at normal incidence onto the surface of the sample using a cylindrical lens with a focal length of 75 mm. A focused ellipse laser spot with a long axis size of 12 mm and a short axis size of 8.28 μm on the sample surface was obtained. In order to realize large area and efficient processing, the laser scanning direction was perpendicular to the long axis direction of the cylindrical lens, and a large area of micro/nano structures were fabricated with a one-time scanning.

Studies have indicated the surface patterning was dependent on the laser polarization direction, showing that it was beneficial to forming continuous, ordered, and better-controlled micro/nano structures when the writing direction was parallel to the laser polarization [33]. So, the laser scanning direction was parallel to the laser polarization in our experiment. All laser ablation experiments were performed in air.

After femtosecond laser irradiation, all the silicon wafers were rinsed in an ultrasonic cleaner with acetone, ethanol, and deionized water for 10 min, respectively. The surface morphologies of samples were observed using a scanning electron microscope (Hitachi, Japan) measurements. The optical properties of the surface structures were determined with ultraviolet spectrophotometer (Shimadzu, Japan).

## 3. Results and discussion

### *3.1. Formation of micro/nano structures from LIPSSs on the silicon surface*

Fig. 2 illustrates the evolution of the micro/nano structures on the silicon surface under different laser scanning velocities with the

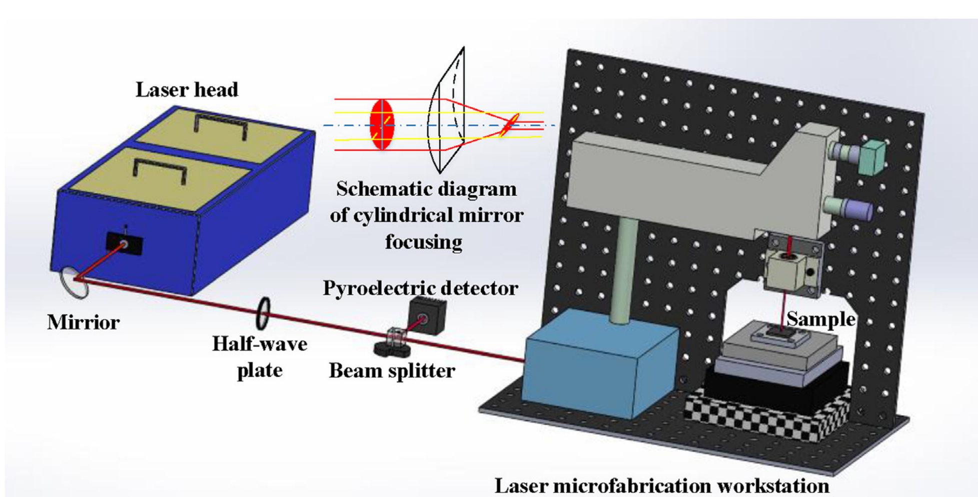


**Fig. 1.** Schematic diagram of the experimental setup.