Reflectivity of Different Texturing Structures Fabricated by Femtosecond Laser Etching

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Abstract - Femtosecond laser etching is applied to fabricate cylindrical, quadrangular and circular hole micro-structures to explore the variation patterns of their reflectivity. The results show that the cylindrical and quadrangular texturing structures have the optimal anti-reflection effect (the reflectivity is always below 6%) in the wavelength range of 350-1000 nm, which is of reference value for the study of fabricating low-reflectivity texturing on monocrystalline silicon surfaces.

1. Introduction
Crystalline silicon solar cells occupy more than 90% of the photovoltaic (PV) market for the advantages of abundant reserves, green nature, mature technology, and large market volume. However, the indirect bandgap of crystalline silicon, low absorption coefficient and high reflectivity at the silicon-air interface (showing reflectivity of about 35-40% in the 300-1100 nm wavelength region) hinder effective light collection [1], resulting in considerable optical losses in crystalline silicon solar cells [2]. Therefore, various surface texturing techniques that can directly improve the photoelectric conversion efficiency of crystalline silicon solar cells have been proposed [3-6] to enhance light trapping and reduce surface reflectivity.

At present, the techniques for fabricating micro-nano texturing mainly include laser etching and wet chemical etching [7-10]. Laser etching techniques are drawing more and more attention to crystalline silicon surface texturing because of their advantages of the open process environment, uniformity and high precision and controllability [11 12]. In recent years, a variety of anti-reflection structures such as pyramids, honeycombs and V-grooves have been fabricated by laser processing. For example, Choi et al. obtained conical grooves about 10 μm in depth and 10 μm in diameter on the surface of crystalline silicon using an ultraviolet (UV) laser of 355 nm wavelength. After de-slagging and chemical etching, the V-cross section micro-structures were regularly arranged on the surface into a honeycomb structure with a reduced surface reflectivity of 3.3% [13]. Nguyen et al. used the nanosecond laser to etch silicon wafers covered with monolayer self-assembled polystyrene nanospheres, forming nanocone micro-structures with periodic low reflectivity, on the principle that the photothermal interaction between the laser and periodic silicon nanostructures can raise the temperature of the irradiated periodic silicon nanostructures enough to induce their thermal shaping [14].

Laser texturing has the potential for lower reflectivity and low-cost production. Currently, laser texturing focuses on improving surface micro-structure types and morphology to enhance the anti-reflection effect. This paper investigates and compares the reflectivity variation patterns and anti-
reflection mechanisms of cylindrical, quadrangular and circular hole microstructures fabricated by femtosecond laser etching in an air environment. The results show that the anti-reflection effect of monocrystalline silicon is substantially enhanced in the wavelength range of 350 - 1,000 nm, which provides an option for improving the photoelectric conversion efficiency of silicon-based solar cells.

2. **Experiment**

2.1 Sample fabrication
In this experiment, commercially available P-type monocrystalline silicon (100) with a thickness of 500 μm and a resistivity of 1-10 Ω·cm is used. Before laser processing, the monocrystalline silicon is first immersed into anhydrous ethanol for ultrasonic cleaning for 5 min. After being taken out, it is cleaned with deionized water to remove particles and organic contaminants. Then it is placed in the hydrogen fluoride (HF) solution with a mass fraction of 10% and immersed for 5 min to remove the oxide film on the surface of the monocrystalline silicon. At the same time, the metal ions attached to the oxide film surface are also dissolved into the cleaning solution, achieving the purpose of double removal. After being taken out, it is cleaned with deionized water, air-dried and set aside for use.

A femtosecond laser micro-nano precision processing system is used for laser texturing on surfaces. As shown in Figure 1, (a) is the machine picture and (b) shows the corresponding optical path. The processing system comprises a water cooling system, femtosecond laser, frequency multiplier module, beam expander, reflector, galvanometer scanner and computer. The laser parameters include a wavelength of 520 nm, a pulse width of 400 fs, a repetition frequency of 100 kHz, and a spot diameter of 20 μm.

![Figure 1. Femtosecond Laser Precision Micromachining Equipment (a) Machine, (b) Optical Path](image1)

![Figure 2. Schematic Diagram and Scanning Tracks of Several Texturing Structures Fabricated: (a) Cylindrical, (b) Quadrangular and (c) Circular Hole Micro-structures](image2)
Figure 2 shows the laser scanning tracks (partial) of a cylindrical, quadrangular, circular hole, pyramidal and V-shaped microstructures fabricated by femtosecond laser etching on monocrystalline silicon surfaces. The scanned area of the first three micro-structures is a dark-filled region, which is scanned mainly in two ways: one is cross grooves with a spacing of 10 or 15 μm; the other is array circles scanned along the circle boundary (diameter D). The scanned area of structure (a) is outside the array circles and consists of cross grooves with a spacing of 10 μm and the array circle boundaries; the scanned areas of structures (b) and (c) are inside the array circles and consist of cross grooves with a spacing of 15 μm and 10 μm and the array circle boundaries, respectively. When fabricating these three micro-structures by femtosecond laser etching, the cross grooves are first scanned from the lower-left corner of the sample along the direction perpendicular to the scanning direction, followed by scanning the array circle boundaries starting from the lower-left corner from left to right and from top to bottom. In order to fabricate these types of texturing structures, the laser processing parameters for several micro-structures are finally determined through pre-experiments in combination with the femtosecond laser processing conditions, respectively: (a) cylindrical type: D = 40 μm, d1 = 60 μm, and the number of scans is 5; (b) quadrangular type: D = 40 μm, d2 = 55 μm, and the number of scans is 25. D is the diameter of the circle in the scanning track. For cylindrical, quadrangular and circular hole microstructures, D is equal. d1, d2 and d3 are the distances between adjacent circles in the scanning track for the three micro-structures, respectively, and d4 and d5 are the scanning spacings for pyramidal and V-shaped micro-structures, respectively. For all texturing samples, the scanning speed is 900 mm/s, the frequency is 30 kHz, the average output power of the femtosecond laser is 9W, and the processing area is 5 × 5 mm². The textured samples are placed in a beaker containing anhydrous ethanol for 5 min, cleaned with deionized water, and then picked up with tweezers on the experimental table to dry up naturally for further testing.

2.2 Sample characterization
The morphology of laser-etched monocrystalline silicon micro-structures is obtained using a field-emission scanning electron microscopy (FESEM, JSM-6500F, Jeol Co. Japan). Geometric profiles are drawn using a 3D laser scanning confocal microscope (OLYMPUS, OSL4100, Japan). The reflectivity in the UV, visible and NIR (350-1000 nm) regions is characterized by a spectrophotometer.

3. Results and Discussion

3.1 Morphology of micro-structures

Figure 3 shows the laser confocal 2D images of a cylindrical, quadrangular, circular hole, pyramidal and V-shaped microstructures fabricated by femtosecond laser etching. With the short action duration and high energy, the femtosecond laser etching rapidly melts and vaporizes the target material, thus removing the local material and forming the above-mentioned micro-structures. The 2D images show that all the five texturing structures are uniformly distributed with approximately equal spacing. In Figure 3 (a) Cylindrical Micro-structure, it can be observed that local melting creates relatively small
size micro-structures during repeated scanning by the femtosecond laser (as shown in the black dashed
circles pointed by the black arrows). In Figure 3(b) Quadrangular Micro-structure, similarly, micro-
structures of smaller size are formed locally (as indicated by the white dashed circles pointed by the
white arrows shown in the figure). The circular hole micro-structure in Figure 3(c) is obtained by
increasing the distance between adjacent circles (dark-filled areas) in the laser scanning track in Figure
3(b). Small size micro-structures are observed inside some of the circular holes (as indicated by the gray
dashed circles pointed by the pink arrows shown in the figure), the reason for which may be that the
materials melt and vaporize rapidly due to the femtosecond laser irradiation and some of them cannot
be discharged from the blind hole in time, or that small particles from the unetched surface between the
circular hole micro-structures fall into the circular holes during the laser irradiation. On the whole, all
five types of texturing structures fabricated by the femtosecond laser on the monocrystalline silicon
surfaces are uniformly distributed and closely arranged.

Figure 4. 3D Images and Cross-sectional Morphology: (a) Cylindrical Micro-structure, (b)
Quadrangular Micro-structure, (c) Circular Hole Micro-structure.

In order to investigate the geometrical characteristics of different types of texturing structures, the
laser confocal 3D morphological features of the periodically arranged cylindrical, quadrangular and
circular hole texturing structures fabricated by femtosecond laser etching are shown in Figure 4,
respectively. As shown in Figure 4(a), it can be observed that the cylindrical micro-structure has a cross
section with a bottom side diameter of 40 μm, a height of about 75 μm, and a spacing of 55 μm, and a
depth-to-width ratio of 1.9. Figure 4(b) shows the quadrangular micro-structure, and it has a cross
section with a side length of about 40 μm, a height of about 70 μm, a spacing of 55 μm, and a depth-to-
width ratio of 1.7. The circular hole micro-structure is shown in Figure 4(c), which has a cross section
with a diameter of about 40 μm, a hole depth of about 70 μm, a spacing of 70 μm, and a depth-to-width
ratio of 1.7. In terms of the above, the heights or depths of these three types of texturing structures
fabricated by femtosecond laser etching are similar, despite the different number of scans for cylindrical,
quadrangular, and circular hole micro-structures. This is because the energy of the femtosecond laser
expands in space according to the hyperbolic law and decays rapidly after the focus is passed. When the
processing parameters of the laser are the same, and the spot focuses on the surface of the
monocrystalline silicon sample (i.e., the zero point) and remains constant, the laser energy continues to
decay on the longitudinal scale (below the zero point) as the increasing number of scans and the etching depth, resulting in the target material not being continuously removed with the increasing number of scans. Therefore, the longitudinal dimension of a quadrangular micro-structure scanned 25 times is similar to that of a circular hole micro-structure scanned 15 times. Although the cylindrical micro-structure is scanned only five times, the same location is scanned several times due to the small distance between the scanning tracks of the laser cross groove, and eventually, similar longitudinal dimensions to the quadrangular and cylindrical micro-structures are also obtained.

In addition, to further investigate the surface morphological features of several texturing structures by femtosecond laser etching, SEM is used for characterization and analysis. Figure 5 shows the top views and cross-sectional views of the cylindrical, quadrangular, circular hole, pyramidal and V-shaped micro-structures, respectively. From the top views, it can be seen that all five texturing structures are neatly arranged and evenly distributed, and the surfaces are covered with small size micro-structures. Figure 5(a1) is the top view of the cylindrical micro-structure. Small size regular cones and irregular micro-structures exist between the cylindrical micro-structures, which are generated by the melting and vaporization of the material during the femtosecond laser etching process, consistent with the results of the confocal diagram in Figure 3(a). Figure 5(b1) is the top view of the quadrangular texturing structure with "a small open mouth" at the top of each prism, probably due to the thermal stresses accumulated from multiple scans of the femtosecond laser. The spacing between the micro-structures is a circular hole, and small size cylindrical-like micro-structures exist inside the circular hole, which is produced by the melting and vaporization of the material during the laser processing. Figure 5(c1) is the top view of the circular hole micro-structure. The unetched surface between the circular hole micro-structures is covered with smaller-size particle micro-structures, and smaller-size particle micro-structures exist within the local circular hole micro-structures.
The cross-sectional views of the three different texturing structures visualize the size of the micro-structures fabricated by femtosecond laser etching as a whole, further demonstrating the dimensional information obtained by laser confocal diagrams in Figure 4. Moreover, it is found that small-size micro-structures are formed on the surface of all the texturings during laser etching, and no cracks occur inside. For the cylindrical micro-structure, it can be observed from the cross-sectional view that there are regular or irregular micro-structures connected to the cylinder at the bottom of the cylindrical micro-structure, and some of them are spike-like, which are formed by the special scanning tracks of the laser. Moreover, the surface is covered with flaky micro-structures (white dashed boxes pointed by white arrows as shown in the figure), which is the result of some debris generated during the cutting process falling onto the surface of the micro-structures. Smaller-size cylindrical-like micro-structures can be observed between the quadrangular prisms in the quadrangular micro-structure. Finer micro-structures are not observed in the cross-sectional view of the circular hole micro-structures, which, combined with the laser confocal 2D diagram in 3(c), indicates that such finer micro-structures are only randomly present in some circular hole micro-structures. The melt cannot be removed from the hole in time, presumably because multiple laser irradiations make the unetched surface between the circular hole micro-structures covered with small-sized particles, and the bond between these small particles and the monocrystalline silicon surface becomes poor, causing some small particles to fall from the surface into the circular hole.

3.2 Anti-reflection effect

Figure 6. Reflectivity Spectra of (a) Untextured Planar Monocrystalline Silicon and (b) Textured Cylindrical, Quadrangular and Circular Hole Micro-structures.

Figure 6 shows the reflectivity spectra of untextured planar monocrystalline silicon and textured cylindrical, quadrangular, and circular hole texturing structures. It can be observed from Figure 6(a) that the reflectivity of planar monocrystalline silicon is greater than 60% in the wavelength range of 350-390 nm, between 25% and 60% in the wavelength range of 390 - 780 nm, and between 20% and 25% in the wavelength range of 780-1000 nm. Compared with planar monocrystalline silicon, the reflectivity of all five types of texturing structures fabricated by femtosecond laser etching is significantly reduced, further demonstrating that micro-structures play a remarkably important role in increasing the number of reflections of incident light and the optical path and reducing the reflectivity. Figure 6 shows the reflectivity spectra of cylindrical, quadrangular and circular holes. It can be observed that in the whole wavelength range, the circular hole micro-structure (the blue curve in the figure) achieves the lowest reflectivity of 5.5% at a wavelength of 800 nm. Compared to planar monocrystalline silicon, the cylindrical micro-structure has a better anti-reflection effect in the red to NIR waveband. However, its reflectivity is significantly higher than that of cylindrical and quadrangular micro-structures within the whole waveband. On the one hand, the circular hole micro-structure can effectively increase the number of reflection and absorption of the incident light and reduce the reflectivity; on the other hand, the
cylindrical and quadrangular micro-structures have higher density, larger depth-to-width ratio, and are distributed with melting micro-nano structures of smaller size between the micro-structures, which can further enhance the light trapping ability. Therefore, the reflectivity of the two micro-structures is lower than that of the circular hole micro-structure, providing a superior anti-reflection effect throughout the UV to NIR region (reflectivity values are always below 6%). Moreover, the reflectivity of the cylindrical micro-structure (the black curve in Figure 6(b)) is slightly lower than that of the quadrangular micro-structure (the red curve in the figure) in the whole wavelength range. The reflectivity of both micro-structures is close in the wavelength range of 600-775 nm, and only in the wavelength range of 350-600 nm and 750-1000 nm is the reflectivity of the cylindrical micro-structure slightly lower than that of the quadrangular micro-structure. Both micro-structures have smaller-size micro-nano structures as they are essentially similar in size. However, the slightly larger depth-to-width ratio and more dense melting micro-nano structures of the cylindrical micro-structure allow for a slightly lower reflectivity than that of the quadrangular micro-structure.

4. Conclusion
In order to enhance the light absorption on the monocrystalline silicon surface, cylindrical, quadrangular and circular hole texturing structures are fabricated by the femtosecond laser in this paper. The results show that all the three texturing structures fabricated are uniformly distributed and well arranged. Meanwhile, the cylindrical and quadrangular micro-structures have smaller-size micro-structures, yet the former is distributed with more dense melting micro-nano structures. Regarding the optical characteristics, the reflectivity of the textured monocrystalline silicon surface is significantly reduced. In the wavelength range of 350-1000 nm, the surface of cylindrical micro-structures, featuring a slightly larger depth-to-width ratio and higher density of melting micro-nano structures, provides relatively better reflectivity (below 5%). This paper could provide a reference for the research on fabricating low-reflectivity texturing surfaces.

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