

High-efficiency anti-reflection composite micro-nano structures were fabricated on the Si surface using femtosecond laser technology

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Silicon exhibited excellent optical properties in the visible to near-infrared band and had significant applications in optical communication, spectral detection, solar cells, and near-infrared sensors. However, optical devices made of silicon have a serious problem. Silicon has a very high reflectivity in the vision-infrared range, which will seriously reduce the efficiency and sensitivity of light usage. Therefore, in this work, femtosecond laser processing technology was employed to enhance its optical properties and increase its anti-reflection performance. This method fabricated large-area deep microholes, ordered and random, with low damage and low cost silicon microhole arrays. Experimental tests have shown that it has ultra-wideband anti-reflection performance (with a minimum reflectivity of 3.1% from 380 to 1100 nm). This experimental method could control the depth of silicon micropores by regulating the energy of femtosecond laser and the number of direct writes, thereby regulating its optical properties. This silicon deep microholes demonstrated self-cleaning and strong hydrophobic properties (water contact angle $130 \pm 2^\circ$) in the hydrophilicity and hydrophobicity test. The microholes structure of Si exhibited excellent anti-reflection, self-cleaning, and strong hydrophobicity over a wide wavelength range, which was crucial for enhancing the performance of various optical, optical functional, and optoelectronic devices. It had also played a supporting and promoting role in the research and development of photovoltaic devices, COMS devices and spectral detection devices.

Keywords: femtosecond laser technology, anti-reflection, hydrophobic, microholes structure.

1. Introduction

In recent decades, global energy issues have been a rather thorny problem, leading the world to shift towards the use of renewable energy [1]. Sunlight is the most abundant and easily accessible renewable energy source [2, 3]. People can efficiently utilize solar energy by enhancing the reflectivity of materials in the broadband range of visible light to near-infrared [4]. At present, the main method to improve the anti-reflective performance of materials is to apply anti-reflective coatings on the surface. We did indeed draw on the biomimetic design concept of the moth eye structure. The silicon microholes

structure we prepared also has a gradually varying effective refractive index, thereby reducing the reflection of silicon. We have provided additional details in the introduction section [5–7]. Although current anti-reflective coatings can reduce reflection in the visible light to near-infrared range, they still face the problem of coating peeling. Compared with other semiconductor materials such as Si and GaAs, Si features a small coefficient of expansion, high temperature and high pressure resistance, stable chemical properties, and strong overload resistance. At the same time, Si also features excellent compatibility with the semiconductor industry, a narrow bandgap, and infrared transmission. Therefore, Si is widely used in the manufacturing of micro-nano devices, electronic packaging and related industry fields. The polished Si surface has a very high reflectivity, making it difficult to achieve effective light capture. This would limit its photoelectron conversion efficiency in photonic devices, so we constructed a novel micro-nano structure on the Si surface to enable it to achieve a low reflectivity in the broadband spectral range.

The Chattopadhyay research group [8], inspired by the micro-nano structure of cicada wings, has fabricated nano-tip arrays on the surfaces of materials such as silicon and germanium through experimental simulation and dry etching techniques as highly efficient light collectors, achieving extremely low reflectivity and efficient light absorption.

The Li research group [9] has proposed a method for achieving highly ordered metal oxide nanopatterns on polyimide (PI) substrates based on sol-gel chemistry and soft thermal nanoimprint lithography techniques. The periodic nanopatterns provide broadband enhanced light absorption and quantum efficiency. The Li research group has proposed a method for achieving highly ordered metal oxide nanopatterns on polyimide (PI) substrates based on sol-gel chemistry and soft thermal nanoimprint lithography techniques. The periodic nanopatterns provide broadband enhanced light absorption and quantum efficiency.

The Jiang research group [10] used silica colloidal crystals as the primary etching mask to prepare ordered polymer columns with a size much smaller than that of the template silica microspheres. These highly ordered silicon nanocolumns exhibit excellent broadband anti-reflection performance.

During the interaction between laser and Si material, some side effects that endanger the performance of the material may occur, such as heat-affected zones (HAZ), microcracks, point defects, *etc.* [11]. These key factors are all worth considering so as to achieve high-precision ablation of the material [12, 13]. In some applications, altering the surface wetting characteristics of Si is also crucial. For instance, in hazy and sandstorm environments, dust particles can deposit on the surface of anti-reflective devices [14–16]. Then, in high humidity conditions, they will absorb moisture and become moist, and the Si surface with self-cleaning properties will demonstrate its value [17–21]. In this paper, the femtosecond laser grating repetitive direct writing technology is used to construct a micro-holes structure and nanoscale protrusions on the Si surface [22–26]. This structure can significantly improve the anti-reflection performance while enhancing its hydrophobic performance [27].

2. Experimental methods and apparatus

2.1. Experimental samples and material parameters

The Si crystal orientation used in the experiment was $\langle 111 \rangle$, with a size of $10 \text{ mm} \times 10 \text{ mm} \times 0.5 \text{ mm}$. First, the Si surface was cleaned: it was successively placed in deionized water, acetone (AR), and isopropanol (IPA), and ultrasonicated for 15 minutes each. Finally, wash with deionized water and then dry. Experimental operations are conducted in the hundred-level clean area of the semiconductor factory. Personnel must wear clean suits and go through a wind shower before entering to prevent contamination. During the femtosecond laser direct writing process, the pulse of the femtosecond laser was 70 fs, the frequency was 1 kHz, and the objective lens of the femtosecond laser was a 20 $\times$ objective lens. The detailed operation process is as follows: Select a cleaned sample and place it on the 3D displacement stage. The laser power was set to 1.0–7.0 mW, the speed of the displacement table was set to 2–10 K $\mu\text{m/s}$, the cycle was set to 16 μm , and then the number of repeated direct writing (4, 8, 12) was set before the laser direct writing. Finally, after 30 seconds of ultrasonic cleaning with 1% HF, the function of the HF cleaning here is to remove the oxide layer, residual molten substances, *etc.* the silicon microhole structure was prepared.

2.2. Experimental testing methods

The morphology and EDS energy spectrum of micro-nano structures were observed in the experiment using a scanning electron microscope (SEM). The contact angle tester measures by testing the hydrophilic and hydrophobic properties of micro-nano structures with 30 μL of distilled water, the test conditions for the water droplet angle are as follows: standard test temperature $23 \pm 2^\circ\text{C}$, and standard humidity range $45 \pm 10\% \text{ RH}$, and the test is conducted in a clean room. The optical properties of the micro-nano structure of Si are measured by a UV-Visible-near-infrared spectrophotometer. The profilometer was used to test the roughness and depth profile of the sample.

3. The micro-nano structure morphology and forming mechanism of Si prepared by femtosecond lasers of different energies

This section explored the micro-nano structure morphology of the Si surface under different focusing objective and laser power. The experimental parameters in Fig. 1 were the focusing objective of 20 $\times$, NA = 0.4, the laser direct writing speed of 9000 $\mu\text{m/s}$, and the direct writing period of 16 μm . The laser powers were 2.5, 4.5, and 7.0 mW, respectively corresponding to diameters of 2.8, 4.5, and 4.5 μm . The very high peak power of femtosecond lasers could easily cause multi-photon ionization, avalanche ionization and other effects in the laser beam spot area. The energy of the femtosecond laser was deposited in large quantities at the focus in a short period of time. The temperature of the electrons generated instantaneously was much higher than the melting and vaporization temperature of Si material, forming a plasma in an ultra-high temper-

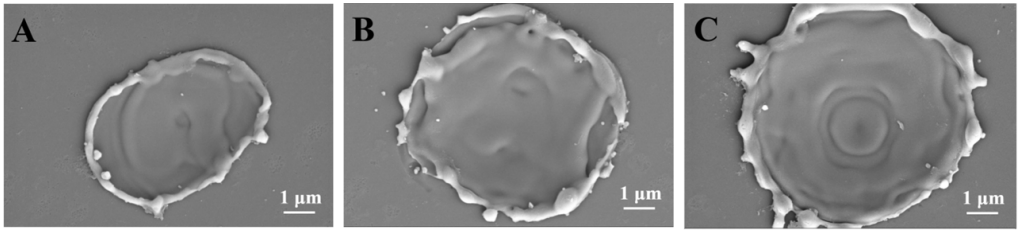


Fig. 1.

ature and ultra-high pressure state. The shock waves generated by ultra-high temperature and high pressure cause part of the molten Si to diffuse outward from the center of the micro-holes, inducing micro-explosions. This led to an increase in the diffusion range of the thermally melted Si. The micro-craters formed under a low-power laser with a power of 2.5 mW present an elliptical shape. Under the direct writing of high-energy femtosecond laser and low-magnification objective lens, the Si surface presents a regular circular micro-holes structure. The original Si surface structure in the laser irradiation area was destroyed, and the ablated molten Si material was pushed by the huge pressure formed by the focused spot to form a rough micro-holes edge. After the laser was applied, the material temperature cooled rapidly and dropped to form a molten casting layer. It could be seen that the diameter of Si micro-holes gradually increased with the increase of laser power. The formed silicon micro-holes present a circular shape, and there were irregular protrusions around the circular micro-holes structure.

4. Research on anti-reflection morphology of Si composite micro-nano structures

4.1. Grating *in situ* direct writing technology

This section explored the surface morphology evolution law and physical mechanism of Si surface composite micro-nano structures fabricated by femtosecond laser grating *in situ* direct writing technology, as shown in Fig. 2. The focusing objective lens used in the preparation of A–C in Fig. 2 was 20 $\times$, with NA = 0.4, A period of 8 μm , a direct writing speed of 3000 $\mu\text{m/s}$, and a laser power of 2.5 mW. The number of direct writes was 4, 8 and 12 times in sequence. When the number of direct writes was 4 times as shown in Fig. 2A, the formed micron grooves were relatively shallow, with only faint grating patterns and a small number of nanospheres remaining on the surface. As the number of direct writing increased to 8 times, the laser beam spot overlap rate formed by low-magnification and high-energy repeated direct writing was greater and the energy was higher. High-energy subsequent pulses would act on the previous pulses, further heating and melting the Si material. The depth of the micrometer slots increased, while the number of surface nanospheres relatively decreased, thus forming the prototype of a micrometer-scale grating slot as shown in Fig. 2B. There were still pits of femtosecond beam spot ablation on the inner side of the grating, which was the effect produced

by the repeated action of femtosecond pulses on the same point during multiple direct writing processes. The subsequent femtosecond laser pulses would remelt the previously formed nanospheres and pushed them to both sides of the beam spot trajectory to form a cast. The subsequent femtosecond laser pulses would remelt the previously formed nanospheres and push them to both sides of the beam spot trajectory to form a cast. When the number of direct writes was 12 times, the depth of the grating slot further increased, and no nanospheres or voids appear in the grating ridge and slot, as shown in Fig. 2C. Grating structures formed by high-energy laser ablation, sputtering and solidification appeared in the grating grooves. Meanwhile, the depth of the grating grooves also increased accordingly, and there were some rough nanoscale textures on the grating ridges, which were formed by the repeated hot melting, recasting and accumulation of the molten castings.

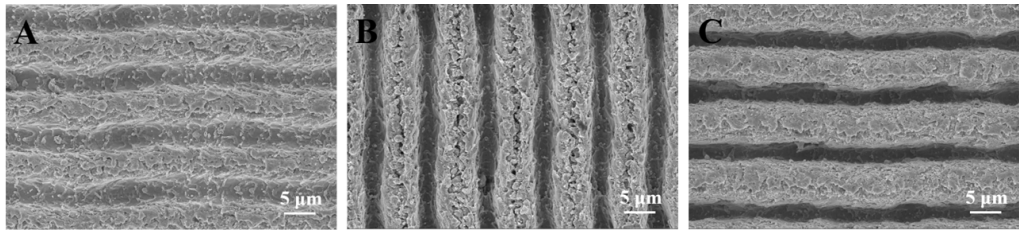


Fig. 2.

Because during the ablation process of silicon by high-energy-density femtosecond pulsed lasers, the laser energy irradiates the silicon sample, caused its surface to rapidly heat up and melt. Strong interactions occurred on the material surface, such as Coulomb explosions and nonlinear absorption effects, accompanied by the eruption of molten materials. The high temperature and pressure formed by the high-energy femtosecond laser cause the Si surface to melt, and the molten material is pushed to both sides of the beam spot scanning trajectory and solidifies to form a cast layer.

4.2. Orthogonal *in situ* direct writing technology

Orthogonal *in situ* direct writing technology referred to the direct writing on the sample surface by two femtosecond laser beam spots with mutually perpendicular scanning directions. The orthogonal direct write times of Fig. 3 A–C were 8, 16, and 24 times in sequence. When the number of orthogonal direct writes was low, as shown in Fig. 3A, the trajectory after laser irradiation destroys the surface structure of the sample, and only regular grooved structures were presented on the Si surface. Due to the low number of orthogonal direct writes and less energy accumulation, there were some regular nano-spherical particles in the micro-grooves and on the grid ridges. When orthogonal direct writing was performed 16 times, only micro-groove structures were formed on the surface of the prepared Si samples, without the formation of large-area regular micro-holes structures, as shown in Fig. 3B. The formation of microgrooves was due

to the fact that more laser pulses and energy were obtained at the same position, which would increase the temperature within the laser irradiation area and trigger a more intense ablation and ablation phenomenon. When the number of orthogonal direct writing increased to 24 times, a clear microholes structure appeared on the sample surface. The high-energy *in situ* orthogonal direct writing gradually disappeared the groove structure and transformed it into a densely distributed microholes structure, as shown in Fig. 3C. However, the recast layer around the micro-holes was damaged. This might be due to the shaking of the sample stage during processing, which caused the laser beam spot to shift and the resulting high temperature and high pressure damaged part of the recast layer around it. Among them, the formation reason of the grating ridge was that the focused light spot does not act on this area during the laser direct writing process. Or when the focused light spot passes through the irradiation area, the ablated Si material was pushed to both sides of the scanning path by the huge energy formed by the focused beam spot, resulting in new ablation and recasting. It was well known that shallow microholes structures offer fewer multiple reflection processes, resulting

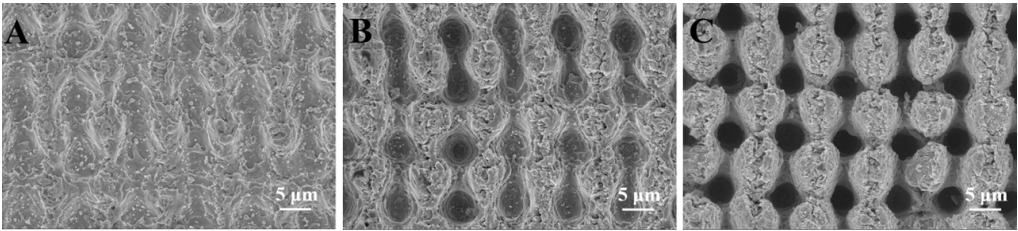


Fig. 3.

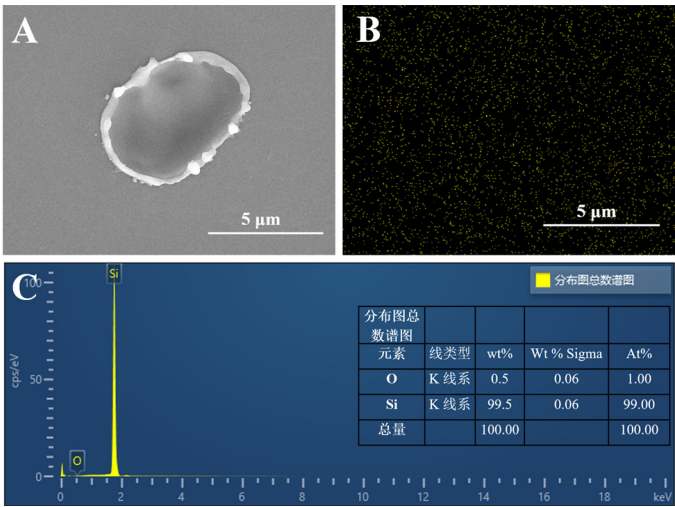


Fig. 4.

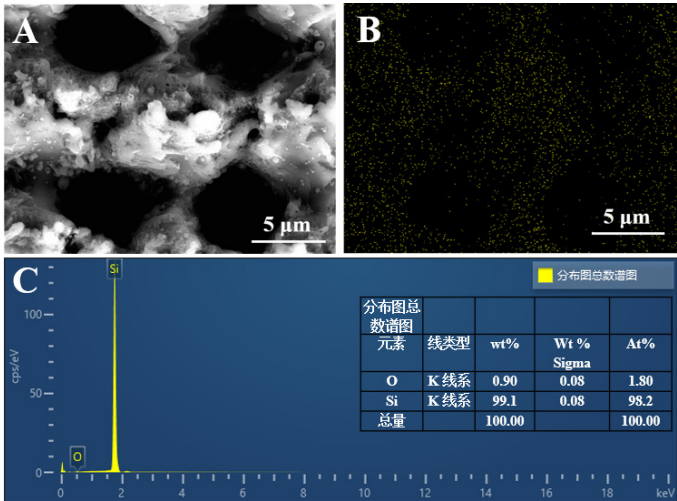


Fig. 5.

in a relatively weak ability to capture scattered light. A deeper microholes structure could form more efficient anti-reflection performance.

This section analyzed and tested the microhole structure in Fig. 1 and the microholes in Fig. 3C, as shown in Fig. 4. The weight ratios of Si to O in a single microhole are 99.5% and 0.5%, respectively, as shown in Fig. 4C. This was because a thin oxide layer was formed when the sample was exposed to the air, and some O elements were also carried in the recast layer. However, during multiple direct writing processes, the irradiated areas of the perpendicularly intersecting beam spots would overlap and undergo molten recast. Meanwhile, silicon reacts with oxygen in the air to form silicon oxide, with the weight ratios of Si and O being 99.1% and 0.9% respectively, as shown in Fig. 5C. Moreover, the O element was concentrated on both sides of the scanning path, mainly because the femtosecond laser beam spot pushes the molten Si to both sides of the beam spot. It could be found from Figs. 4 and 5 that as the number of laser scans increases, the probability of oxidation reactions in the material also increases, which leads to an increase in the weight ratios of O. Moreover, the high temperature and pressure generated by the femtosecond laser would prevent a portion of the silicon oxide encapsulated in the recast layer from being removed by HF.

5. Research on the anti-reflection and hydrophilic and hydrophobic properties of composite micro-nano structures

The ultraviolet-visible-infrared spectrophotometer during the testing process achieved spectral testing in the wide band of 380–1100 nm by automatically switching light

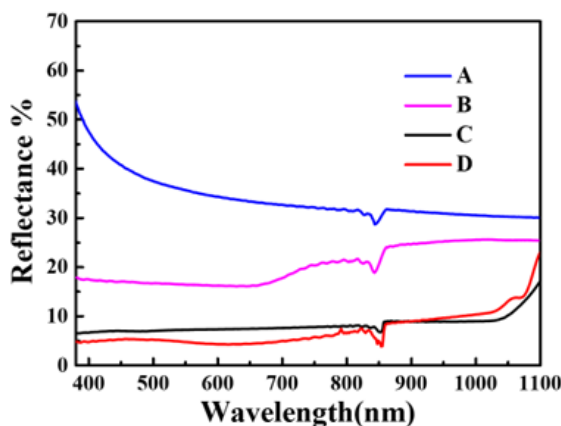


Fig. 6.

sources of different spectral ranges. This instrument uses a halogen lamp as the light source for visible light and an indium lamp as the light source for near-infrared light. The switching of their light sources occurs at a wavelength of 860 nm, resulting in a discontinuous curve. The average reflectance of the Si composite micro-nano structure was significantly lower than that of the original Si sheet, as shown in Fig. 6. As the number of laser direct writes increased, the reflectance also showed a gradually decreasing trend. The average reflectance in the 380–1100 nm band is 4.6%, and the lowest reflectance was 3.1% (after 24 times laser direct writes). The experiment also tested the water contact angles of the composite micro-nano structures. Their hydrophobic angles were $70 \pm 2^\circ$, $61 \pm 2^\circ$, $95 \pm 2^\circ$, and $130 \pm 2^\circ$, respectively, corresponding to 8, 16, and 24 times of direct writing. It could be found that as the number of laser direct writes increases, the hydrophobic Angle of the composite micro-nano structure gradually increases. This was because the number of direct writes increases, and the hole depth of the composite micro-nano structure formed on the Si surface increases significantly. Moreover, the ridge had a more refined hierarchical micro-nano structure, which increases the hydrophobicity of the sample. Therefore, the Si composite microstructures prepared by femtosecond laser *in situ* repetitive direct writing technology have excellent superhydrophobicity and can achieve a very good self-cleaning effect. This broadened the application fields of Si composite micro-nano structures, which can be widely used in solar thermal devices.

6. Conclusion

In this paper, femtosecond laser direct writing technology was used to fabricate Si composite microholes structures. A large number of regular Si composite micro-nano structures were successfully fabricated by controlling the energy of femtosecond laser and the direct writing method, and the variation law of the morphology of Si micro-nano structures was studied. The micro-pits formed under high-energy-density lasers pres-

ent a circular shape, and there will be irregular recast layers around the micro-pits. As the number of femtosecond laser direct writes increased successively, the depth of the formed microholes gradually increased, while the reflectance showed a gradually decreasing trend. The average reflectance was 4.6%, and the lowest reflectance was 3.1% (24 times direct writes) in the 380–1100 nm band. The silicon composite micro-nano structure also had a relatively high hydrophobic angle of $130 \pm 2^\circ$. Therefore, Si composite micro-nano structures were fabricated by femtosecond laser technology, achieving excellent anti-reflection effects and outstanding hydrophobic properties over a wide spectral range. These characteristics make this type of silicon composite micro-nano structure have great potential for application in fields such as solar cells, outdoor displays and sensors. For instance, the wide-spectrum anti-reflection property can enhance the photoelectric conversion efficiency, while the hydrophobic property can increase the outdoor stability and durability of the devices.

Credit authorship contribution statement

Yi Yang: conceptualization, data curation, investigation, validation, writing – original draft, writing – review and editing. Yajin Che: data curation. Hao Lei: data curation, validation. Yi Yang: supervision, resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data will be made available on request.

Acknowledgements

This work was supported by Research on Agricultural Multi-Element Data Collection Station Based on Cloud Platform (No. 2023KC05).

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*Received December 8, 2025
in revised form January 24, 2026*