International Journal of Energy
ISSN: 2957-9473 | Vol. 2, No. 1, 2023

Evolution of structured silicon after picosecond laser irradiation

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Abstract: We prepare the black silicon by directly irradiating crystalline silicon with picosecond laser pulse in atmospheric environment. The grating scanning mode is used in the irradiation process and a regular 20 μm × 20 μm square grating are obtained on the silicon surface. The evolution of surface microstructure with the change of scanning speed and laser pulse energy is preliminarily studied. When the pulse energy is 4.78 μJ and scanning speed is 200 mm/s, picosecond laser can achieve drilling a hole on silicon surface, and the hole will become larger as the the number of pulses increases. In addition, laman spectra is measured and results show picosecond laser processing does not change the crystal phase.

Keywords: Surface modification; Picosecond laser; Silicon; Laman spectra.

1. Introduction

As an important semiconductor material in the electronic industry, crystalline silicon is widely used in the fields of large-scale integrated circuits and solar cells due to its rich crustal content, high temperature resistance, easy doping, non-toxic and pollution-free, and easy integration with existing CMOS processes [1,2]. However, monocrystalline silicon has a high reflectance of more than 40% in the band of 0.25~2.5μm, which seriously affects the performance of silicon-based photodetectors and the efficiency of silicon solar cells. In addition, the band gap width (1.12eV) of crystalline silicon determines its narrow spectral absorption, thus limiting its application range. In order to break through the limitation of existing silicon-based photoelectric devices and improve the efficiency of existing silicon solar cells, the modification technology of silicon materials is worth further exploration and research [3].

One idea of silicon material modification is to modify its surface to solve the problem of low absorption of crystalline silicon in the visible and near-infrared bands. At present, the main methods for surface modification of crystalline silicon include ultrashort pulse laser processing [4,5], metal-assisted chemical etching [6,7] and reactive ion etching [8]. The silicon modified by these methods is also called "black silicon". In the preparation process of black silicon based on ultrashort laser pulse, the nonlinearity of laser pulse is mainly used to complete many physical processes such as energy deposition, surface morphology reconstruction and element doping in a very short time [9]. Most of the laser pulses used to process the silicon in the existing reports are femtosecond laser or nanosecond laser. Femtosecond laser can induce periodic micrometer-sized cone structures in and atmosphere of SF_6 [10], however, after the crystalline silicon is irradiated by nanosecond laser pulses in the SF_6 atmosphere, cavities, spherical particles, and irregular protrusions are left on the surface [11]. In this paper, we attempt to use picosecond laser system with a wavelength of 1064nm to process crystalline silicon, and investigate the effects of scanning speed and laser pulse energy on morphology and crystallinity of silicon surface.

2. Experimental setup and methods

The experiment system was performed using an optical fiber picosecond laser (Bellin Laser formula, Amber NX IR-10), which can emit 8.7-ps, 1064 nm laser pulse with repetition frequency of 2000 KHz. In order to scan samples quickly and accurately, the system is equipped with a computer-controlled three-dimensional moving stage as shown in Figure 1. After laser being emitted, the laser beam sequentially passes through collimator lens, halfwave plate, and laser polarizer, and then is rotated by 90° through a mirror, finally focused onto the silicon surface located on sample stage. According the monitoring of a CCD camera, the spot diameter of the ps-laser pulse was about of 20 μm after focusing. The intensity of laser pulse incident on the sample is controlled by a halfwave plate and a linear polarizer. The halfwave plate plays a role in changing the linear polarization direction of the incident laser, and the linear polarizer plays a role in detecting the polarization. The combination of the two can continuously adjust the intensity of the incident light. In this study, the energy of single laser pulse was selected as 2.9 μJ and 4.78 μJ respectively.

N-type (100) silicon wafers with a size of 10 mm × 10 mm, a resistivity of 8-10 Ω cm, and a thickness of 520 μm were cleaned by RCA standard cleaning procedure for surface modification. The cleaned wafers were fixed on the three-dimensional moving stage, and then scanned in a grid scanning mode. That is, the sample was scanned line by line in X direction and then line by line in Y direction, and stepped 20 μm vertically after each line is scanned. In order to explore the effect of the pulse number on surface processing, we have tried different scanning speeds with 100 mm/s and 200 mm/s. The color and morphology of the ps-laser processed silicon was observed by an optical microscope and a scanning electron microscopy (SEM). Reman spectra were recorded with Thermo's DXR Raman microscope using 780 nm laser.

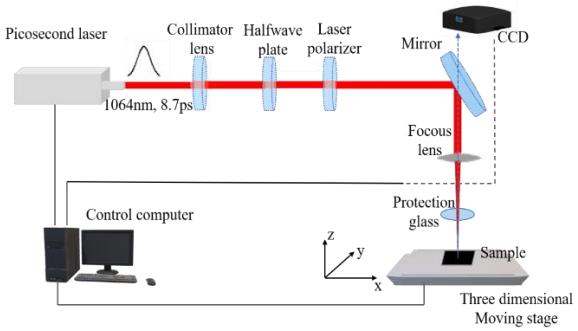


Figure 1. Experimental setup for picosecond laser processing of silicon

3. Results and discussion

The optical microscope images of samples prepared by picosecond-laser pulses with different scanning speeds at different energies are given in Figure 2. It can be clearly seen from the figure that after picosecond laser irradiation the silicon surface color has changed from original gray to dark gray. With the increase of laser pulse energy and the decrease of scanning speed, the surface was turned into black, which implies the silicon surface property might change after laser treatment.

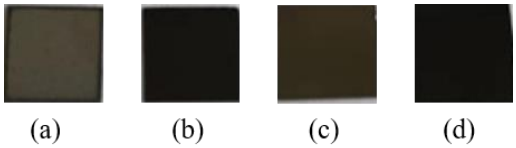


Figure 2. Optical microscope images of samples prepared with different scanning speeds at different incident laser energies: (a) 2.9 μJ and 200mm/s; (b) 2.9 μJ and 100 mm/s; (c) 4.78 μJ and 200mm/s; (d) 4.78 μJ and 100mm/s

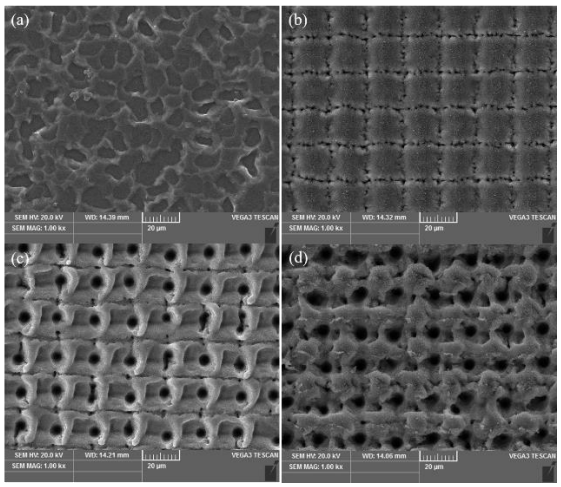


Figure 3. SEM images of samples prepared with different scanning speeds at different incident laser energies: (a) 2.9 μJ and 200mm/s; (b) 2.9 μJ and 100 mm/s; (c) 4.78 μJ and 200mm/s; (d) 4.78 μJ and 100mm/s

The SEM images of picosecond laser treated samples prepared with different scanning speeds at different incident laser energies are given in Fig. 3. When the pulse energy is 2.9 μJ and the scanning speed is 200 mm/s, due to the limitation of the energy threshold, surface ablation rather than volume ablation is mainly produced during the laser interaction with silicon, resulting in irregular shallow holes on the silicon surface. As the scanning speed slows down, the average number of interacting laser pulses per unit area increases and the volume ablation begins to appear. When the pulse energy is still 2.9 μJ and the laser scanning speed drops to 100 mm/s, the laser induces a very regular 20 μm × 20 μm square grating on the silicon surface after scanning in grating format as shown in Figure 2(b), and the laser scanning line is accompanied by relatively small caves. As the laser pulse energy increases to 4.78 μJ, the square gratings remained and a larger cavity appeared in each grid as shown in Figure 2 (c) and Figure 2(d). Comparing Figure 2 (c) and Figure 2(d), it can be seen that under the condition of the same pulse energy, the slower the scanning speed, the larger the cavity is. The main reason for this phenomenon is that hundreds of thousands of laser pulse ablation of a silicon target can lead to drilling a hole [9].

Raman analysis were conducted to study the crystalline phase of the picosecond laser treated samples, and the test results are compared with the Raman spectra of untreated monocrystalline silicon as shown in Figure 4. Figure 4 shows that all picosecond laser treated samples have only one strong Raman peak centered at 511 cm-1, which completely coincides with the peak of untreated monocrystalline silicon. Other peaks corresponding to the amorphous phase do not appear in the Raman spectrum, indicating that the picosecond laser machining of silicon does not cause a phase transition. However, the backscattered light intensity recorded by the Raman spectrum is affected by the laser machining parameters. Because some holes are produced in the process of picosecond laser machining, with the increase of laser energy and number of pulses, the holes become larger and deeper. As a result, the recorded scattered light intensity becomes weaker due to the photons trapping into the hole.

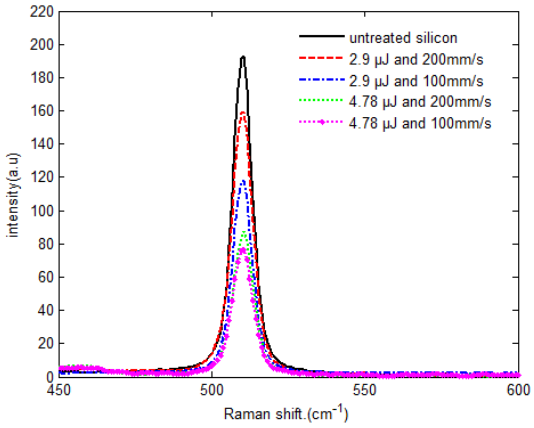


Figure 4. Raman spectra of untreated silicon and samples prepared with different scanning speeds at different incident laser energies

4. Conclusion

Picosecond laser irradiation on silicon surface produces various surface modifications on silicon surface, which are related to the laser scanning mode, the laser pulse energy and the number of pulses. In this paper, a very regular 20 μm × 20 μm square grating are formed on the silicon surface after scanning in grating format. Furthermore, picosecond laser processing can achieve drilling a hole on silicon with the pulse energy of 4.78 μJ and scanning speed of 200 mm/s, and the hole will be larger with the increase of the number of pulses. Finally, Raman spectroscopy shows that picosecond laser processing does not change the crystalline phase of silicon.

Acknowledgements

This work was financially supported by Science and Technology Support Program of Sichuan Province (Grant No. 2021YFSY0049).

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