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The fabrication and characteristic investigation of microstructured silicon with different spike heights

Yan Peng, YunYan Zhou, XiangQian Chen, YiMing Zhu*

Shanghai Key Lab of Modern Optical System, Engineering Research Center of Optical Instrument and System, University of shanghai for Science and Technology, No. 516 JunGong Road, Shanghai 200093, China

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ABSTRACT

Microstructures with different spike heights are fabricated on the silicon surface by using femtosecond laser pulses. It is proved that the spike height of microstructured silicon has specific relations with fabrication parameters, including single pulse energy, pulse number, proportional relation between single pulse energy and pulse number under the same laser fluence, and ambient gas. Additionally, the light absorptions of microstructured silicon with different spike heights are compared. All these results are important for the optimal fabrication of surface-microstructure photovoltaic materials, such as solar cell, infrared sensor, etc.

1. Introduction

Microstructured silicon fabricated by femtosecond laser pulses can change the properties of single crystal silicon material dramatically [1,2]. Importantly, the light absorption property in a wide wavelength range (200–2500 nm) can be enhanced to more than 90% [3,4], which can be widely applied in solar cells [5], infrared sensors and optoelectronic detectors [6,7]. Therefore, many efforts have been devoted to the investigation of surface morphology and absorption property of microstructured silicon under different laser parameters and fabrication conditions, including the laser pulse duration [8,9], laser polarization [10], laser fluence [11], laser wavelength [12], gas medium and the gas pressure [13]. However, little investigations are about the evolution of spike height. According to the investigations before [14], the higher spike height can couple more incident light into the silicon, i.e., enhance the antireflection effect. Moreover, the multi-reflection of light between spikes are beneficial for improving the absorption from doping in the silicon substrate. Importantly, the geometric shape of spikes will not be changed during the later annealing processes, which is indispensable during the manufacture of solar cells or infrared sensors—such as ohmic contact, electrode preparation and passivation processes. This means that the capacity of antireflection and absorption contributed by spike height can be reserved well, which is important for the improvement of the photovoltaic material efficiency. Therefore, in this paper, we experimentally investigated the average spike height of microstructures as functions of single pulse energy, pulse number, proportional relation between single pulse energy and pulse number under the same laser fluence, and ambient gas.

2. Experimental setup and measuring method

We used a Ti:Sapphire laser system, typically 800 nm, 45 fs, 1 kHz, and the spatial profile of laser spot was nearly Gaussian. After focused by a convex lens ($f = 100$ cm), the laser beam was delivered into the vacuum chamber through a 0.4 mm window. The base pressure of vacuum chamber was less than 10^{-4} Torr, and it can be backfilled with gas. The vacuum chamber was fixed on *X* and *Z*-axes translation stage to realize the two dimensional movement. The (100) silicon wafer (phosphor doped, 500 μm thickness, n type with resistivity between 0.01 and 0.02 Ω cm) in the vacuum chamber was put vertical to the incident direction of laser pulses and before the laser focal spot, in order to avoid the damage of high laser energy to window. Correspondingly, the spot of laser beam irradiated on the sample surface was monitored by a CCD camera (WinCamD-UCD12) and its diameter was set at ~300 μm in the entire experiment by changing the distance between the wafer and the lens. Furthermore, for the intensity adjustment, we used a quarter-wave plate and a polarization beamsplitter to provide linear and adjustable attenuation. A beam shutter (SH05, Thorlabs) was used to control the number of laser pulses. After irradiation, the average spike height of microstructure was measured by using a scanning electron microscope (SEM, Tescan,

* Corresponding author. Tel./fax: +86 21 33773176.
E-mail address: ymzhu@usst.edu.cn (Y. Zhu).

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VEGA II). The height of spikes were read from the SEM pictures, and a factor of $\sqrt{2}$ was multiplied because the sample was titled 45° angle for the measurement. Each value of spike height was the average result of 5 points, and the measuring error was ~1 μm.

3. Experiments and discussions

3.1. Single pulse energy

In the experiments, with ambient gas of SF_6 at a pressure of 500 Torr, we investigated the dependence of average spike height of microstructured silicon on the single pulse energy first. The pulse number was fixed at 1000. The corresponding results are shown in Figs. 1 and 2.

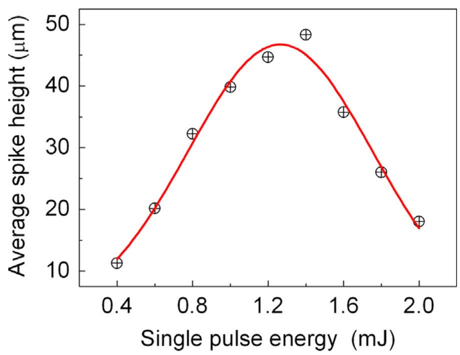

Fig. 1. The average height of spikes as a function of single pulse energy. The circles stand for the experimental data; solid line is the nonlinear fitting curve (Gauss function).

From Fig. 1 we can see that, as the single pulse energy increases from 0.4 to 2 mJ, the average spike height increases first and then decreases, in which the highest spike height can be obtained at the single pulse energy of 1.4 mJ. Usually, the higher the incident laser energy, the stronger the material ablation is. Therefore, it may be thought that the spike height increases with the increase of incident laser energy. However, our experimental results show that when the irradiated pulse number is fixed, there exists an optimal single pulse energy for the maximum of spike height.

For explanation, the entire process of microstructures formation should be considered firstly [15]: when laser beam irradiates on the silicon surface, part of light is scattered by the mirror surface of silicon wafer, which then interferences with the incident beam and results in inhomogeneous energy deposition. The deposited energy ablates and melts the silicon material at non-uniform depth, creating capillary waves. As the increase of ablation and melting time, these capillary waves gradually become ripple pattern, then quasi-periodic array of beads, and finally conical spikes. Therefore, the proper increase of single pulse energy can promote the material ablation and hence contribute to the increase of spike height.

During this process, the single pulse energy determines the ablation and volatilization degree of silicon material; the pulse number represents the interaction time between laser and silicon, which determines how much energy can be transmitted into the material interior. Therefore, when the pulse number is fixed,

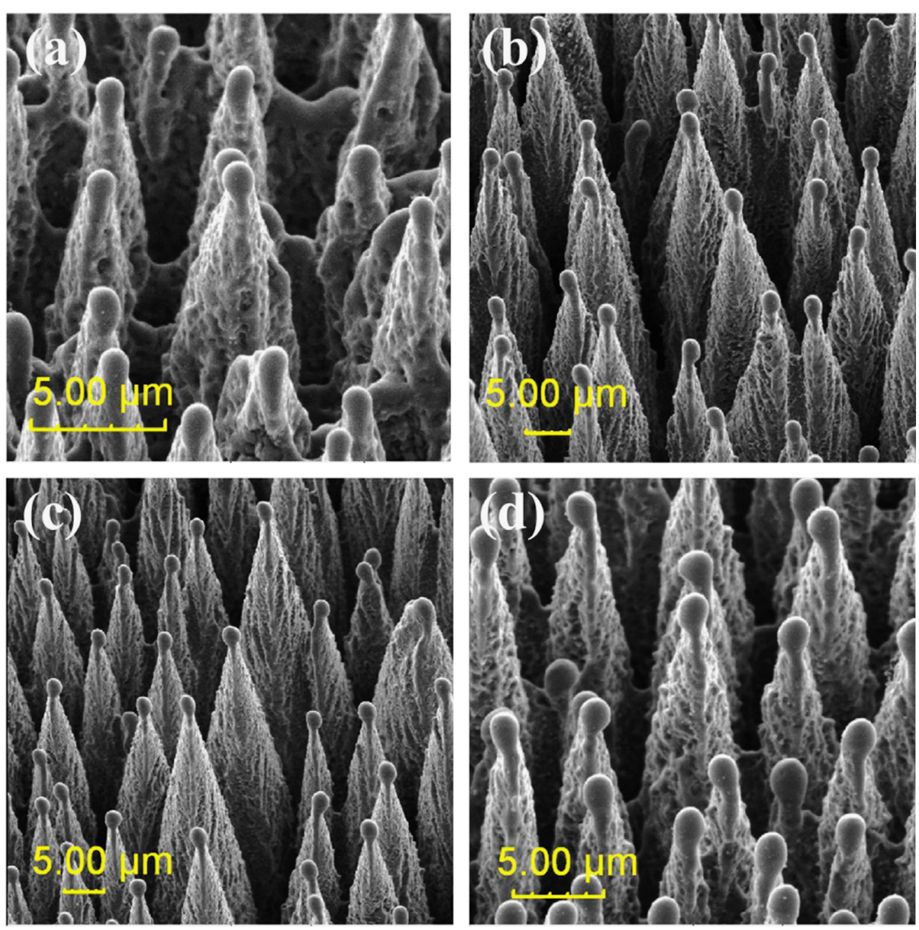

Fig. 2. SEM images of microstructured silicon fabricated with different single pulse energy: (a) 0.4 (b) 1.0 (c) 1.4 and (d) 2.0 mJ. Each SEM image is taken at a 45° angle to the surface normal.

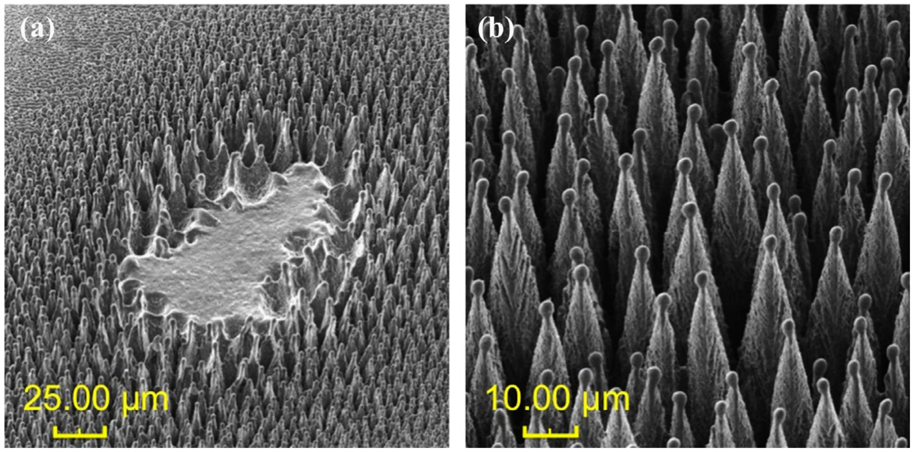

Fig. 3. SEM images of microstructured silicon fabricated with the pulse number of (a) 125 and (b) 1000 under the single pulse energy of 1.6 mJ. Each SEM image is taken at a 45° angle to the surface normal.

energy entered into the interior of silicon in unit time has a maximum. As the irradiated laser energy exceeds the maximum, part of the energy may be accumulated in the topmost layer of silicon material. When the accumulated energy reaches a threshold, the surface material can be excessive ablated to liquid state, and then these spikes cannot be formed during the initial hundreds of laser pulses. In order to prove this, we reduced the pulse number to 125 under the single pulse energy of 1.6 mJ [see Fig. 3(a)]. We can see clearly a melted flat area—liquid state of silicon, instead of conical spikes—is formed in the center of irradiated region. This is the direct proof of energy accumulation and excessive ablation of silicon material. Later, as the increase of time, the energy gradually enters into the interior of material, and then laser pulses can establish spikes again during the later hundreds of laser pulses [see Fig. 3(b)]. In the entire process, the effective energy of laser pulses used for spikes formation decreases. Furthermore, the higher the single pulse energy, the surface ablation effect will be more obvious, and then the effective laser energy is less, the average spike height is lower. For instance, the average spike height in the case of 1.8 mJ is lower than that of 1.6 mJ [see Fig. 1]. As a result, when the single pulse energy exceeds the maximum of transmitted energy permitted by the fixed pulse number, the average spike height decreases with the increase of single pulse energy.

3.2. Pulse number

Similarly, with ambient gases of SF_6 at a pressure of 500 Torr, the changes of average spike height as a function of pulse number (from 100 to 5000) are shown in Figs. 4 and 5 (when pulse number was bigger than 5000, the average height of spikes was still increasing. But the height of spikes cannot be measured exactly because the bottom of spikes were hard to distinguish. Therefore, we stopped the measurement after the pulse number of 5000). The single pulse energy of laser pulses was fixed at 0.4 mJ.

We can see that the average spike height increases monotonically with the increase of pulse number. This is due to that as the increase of pulse number, all the irradiated laser energy has enough time to be transferred into the material interior before the ends of interaction between laser and silicon. This gradually transmitted energy is beneficial for the material ablation and then the spike formation. Therefore, the spike height increases monotonically with the increase of pulse number.

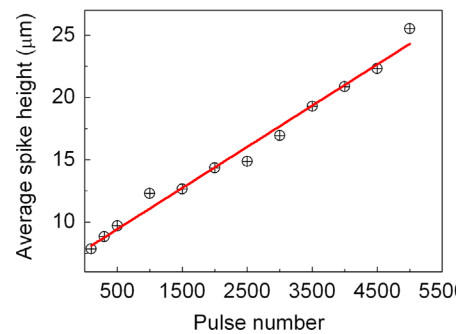

Fig. 4. The average height of spikes fabricated by laser pulses with different pulse number. The circles stand for experimental data; solid line is the linear fitting curve.

3.3. Proportional relation between single pulse energy and pulse number under the same laser fluence

Comparing with the discussions in Sections 3.1 and 3.2, whether the single pulse energy or the pulse number mainly determines the average spike height needs to be investigated further. The laser fluence of femtosecond laser pulse is proportional to the product of single pulse energy and pulse number (pulse number stands for the interaction time between laser and silicon). Therefore, under the same laser fluence of 2.8-kJ/m^2, we measured the average height of spikes formed on the silicon surface under different combinations of single pulse energy and pulse number. The corresponding results are shown in Figs. 6 and 7.

As the single pulse energy increases but not exceed 0.6 mJ, together with the decrease of pulse number, the average spike height gradually increases. When the single pulse energy increases to 0.8 mJ, one flat area emerges in the central part of the irradiated region (Fig. 7(b)), and then the corresponding average height of spikes cannot be measured exactly. When the single pulse energy increases and the pulse number decreases continuously, the range of the flat area enlarges firstly, and then narrows after its area reaches a maximum at the single pulse energy of 1.2 mJ and pulse number of 167 [Fig. 7(c)]. Finally, the flat area completely disappears at the single pulse energy of 1.8 mJ and pulse number of 111 [Fig. 7(d)]. The nonlinear fitting curve in Fig. 6 shows that there also exists a turning point for the microstructure fabrication under different proportional relations between the single pulse energy and pulse number.

This phenomenon can be understood from two aspects: first, when the pulse number is large enough, the laser has enough time to interact with the silicon and then all energy can be transferred into the material interior. Therefore, spikes can be formed effectively, and its average height increases synchronously with the increase of single pulse energy; second, when the pulse number is not enough for all the energy to be transferred into the material interior during the interaction process of laser and silicon, part of the energy can be accumulated in the topmost layer of silicon material. As the accumulated energy reaches a threshold that can melt a large area of surface material, then the melted area can be observed on the silicon surface, i.e., the flat area. While the pulse number decreases to a point that the interaction time between laser and silicon can only support very few energy to be transmitted into material interior, i.e., energy accumulated in the topmost layer is not enough to support the large area melt of silicon material, and then the flat area cannot appear. Correspondingly, the spike height decreases.

3.4. Ambient gas

Usually, these surface-microstructure materials are fabricated in the ambient of sulfur-bearing gases for the reason of that sulfur impurities are beneficial for improving the infrared absorption [13,16]. However, when use this kind of sulfur-contained material for the manufacture of solar cells or infrared sensors, there exists many problems: First, the sulfur-contained material loses its ability of broadband optical absorption after necessary thermal treatment, e.g., ohmic contact formation, electrode preparation and deactivation; Second, after those high temperature processes, isolated substitutional sulfur impurities (optically active state) in the bulk silicon are transformed into sulfur dimer/complex impurities (inactive states), which may act as recombination centers that can capture photo-excited carriers and greatly decrease device photocurrents [17,18]. These problems will greatly reduce the efficiency of optoelectronic devices that employ surface-microstructure silicon.

In order to avoid the problems mentioned above, people try to fabricate similar material in the ambient of vacuum [19–21]. Under these cases, it is found that the antireflection capacity of material can be further increases. At the same time, the infrared absorption from

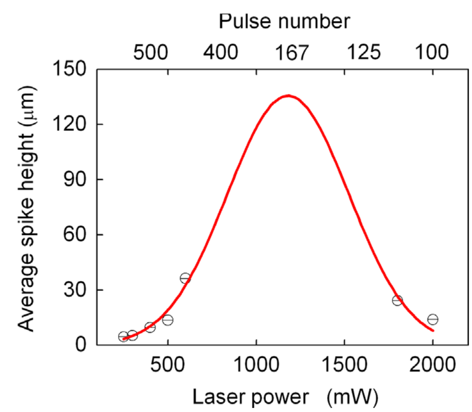

Fig. 6. The average height of spikes fabricated by different combinations of single pulse energy and pulse number under the same laser fluence of 2.8-kJ/m^2. The circles stand for experimental data; solid line is the nonlinear fitting curve (three-parameter exponential function).

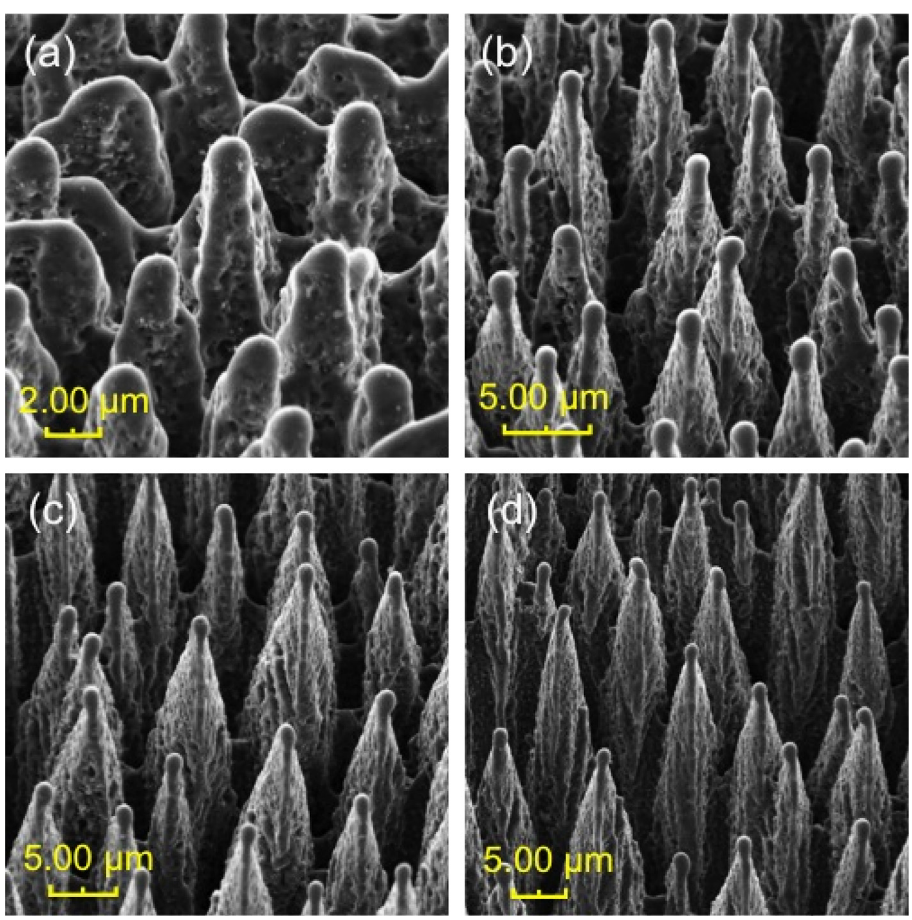

Fig. 5. SEM images of silicon surface after femtosecond laser irradiation with the following number of pulses: (a) 100, (b) 1000, (c) 3000, and (d) 5000. Each SEM image is taken at a 45° angle to the surface normal.

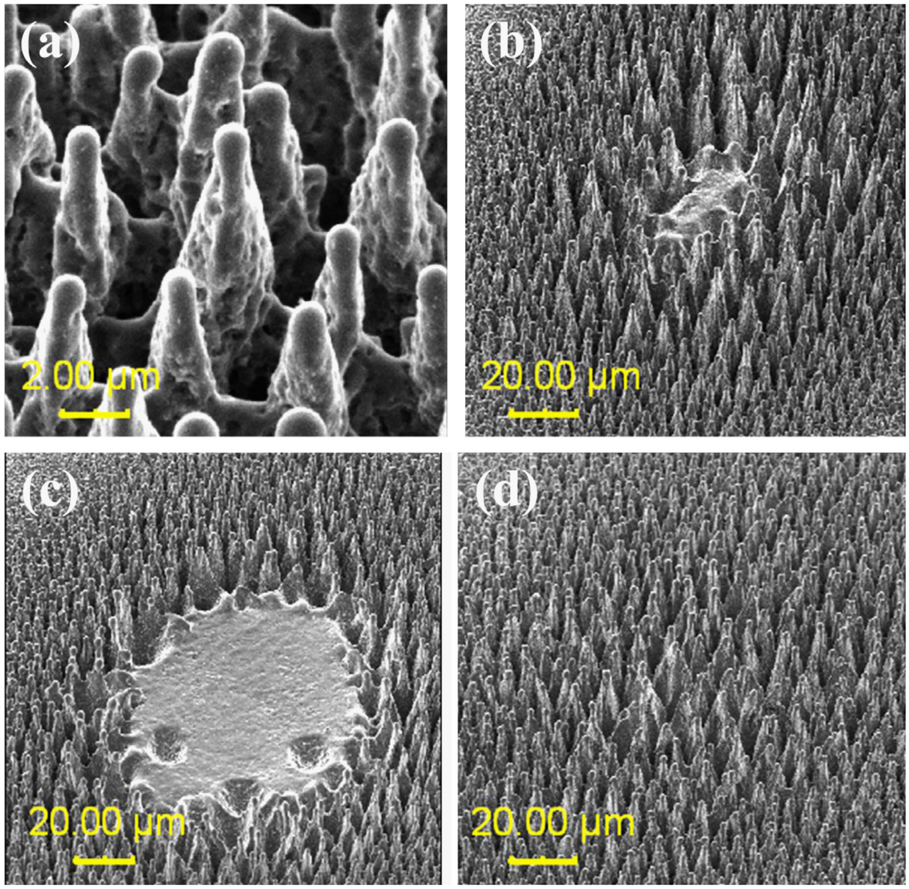

Fig. 7. SEM images of microstructured silicon fabricated with different combinations of single pulse energy and pulse number: (a) 0.4 mJ, 500 pulses (b) 0.8 mJ, 250 pulses (c) 1.2 mJ, 167 pulses and (d) 1.8 mJ, 111 pulses. Each SEM image is taken at a 45° angle to the surface normal.

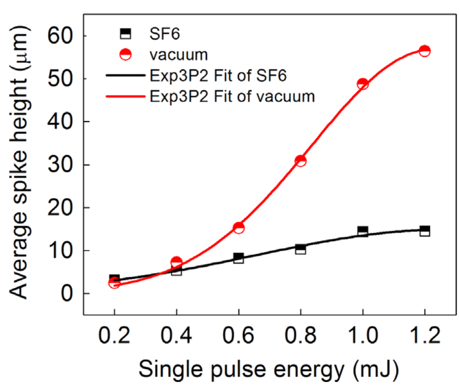

Fig. 8. The average height of spikes fabricated in the ambient gas of SF_6 and vacuum as a function of single pulse energy. The rectangles and circles stand for the experimental data, solid lines are the corresponding nonlinear fitting curves (three-parameter exponential function).

the doping concentration in the silicon substrate can also be enhanced by the multiple reflection of light between spikes. However, there are little investigations about the control of spike height in the ambient of vacuum, especially the quantified analysis. Therefore, the average height of spikes fabricated in the vacuum is investigated here.

In the experiments, the pressure in the case of vacuum was kept at $\sim 10^{-4}$ Torr, while for the case of SF_6, the base pressure was $\sim 10^{-4}$ Torr and then filled back with SF_6 to the pressure of 500 Torr. Here, we just need to compare the difference of spike height under the two ambient gases, thereby the single pulse energy was changed to fabricate spikes with different height. The pulse number was fixed at 300. The corresponding results are shown in Figs. 8 and 9.

Fig. 8 shows that as the single pulse energy increases, the average spike heights under both cases gradually increase and are close to the maximal value permitted by the fixed pulse number. Interestingly, the increase of average spike height in the case of vacuum is much quicker than that of SF_6 gas. Additionally, there are less micro/nano-particles on the surface of spikes fabricated in the vacuum (see Fig. 9). We believe these phenomenon are determined by two reasons: first, the better heat-insulating property of vacuum; secondly, the energy loss in the ionization process of SF_6 gas. Under laser irradiation, the silicon wafer absorbs energy from incident laser pulses. When a sufficient amount of energy is absorbed, the melting and ablative temperature of silicon are reached and an evolution that begins with capillary waves and ripples forms a quasi-periodic array of beads that leads to the formation of conical spikes on the silicon surface [15]. In the gas ambient of SF_6, however, the gas medium absorbs part of the laser energy and dissociates into F ions, which can facilitate a chemical reaction between silicon and SF_6. The higher the laser energy, the more SF_6 molecules are ionized. While in the case of vacuum, all the laser energy is absorbed by the substrate. Furthermore, the better heat-insulating property of vacuum keeps more energy remaining within the bulk silicon, which can facilitate a further increase of spike height. On the other hand, as compared to the chemical etching process between SF_6 and silicon material [13,16], the reaction of silicon in the vacuum are mostly the physical process of melt and cooling, thereby less micro/nano-particles are formed on the surface of spikes.

3.5. Absorption

In order to prove the influence of average spike height on antireflection and light absorption, we measured the absorptance

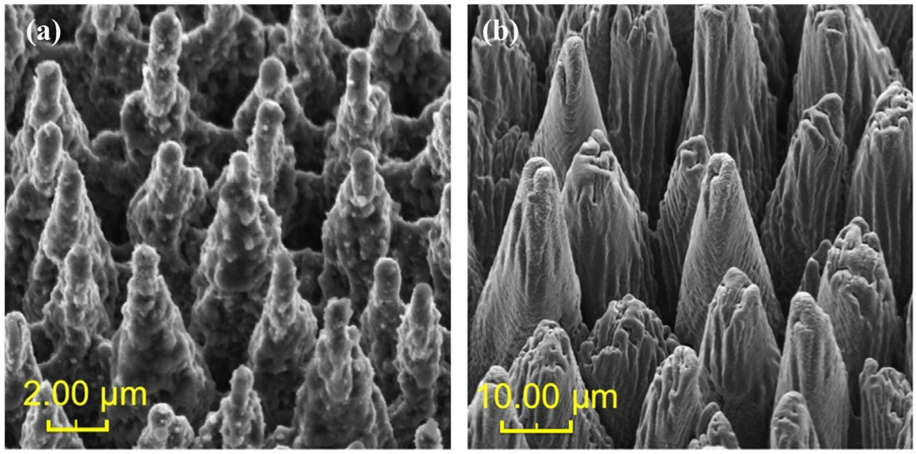

Fig. 9. SEM images of microstructured silicon fabricated in the ambient gas of (a) SF_6 and (b) vacuum. The corresponding single pulse energy is 1.2 mJ and the pulse number is 1000. Each SEM image is taken at a 45° angle to the surface normal.

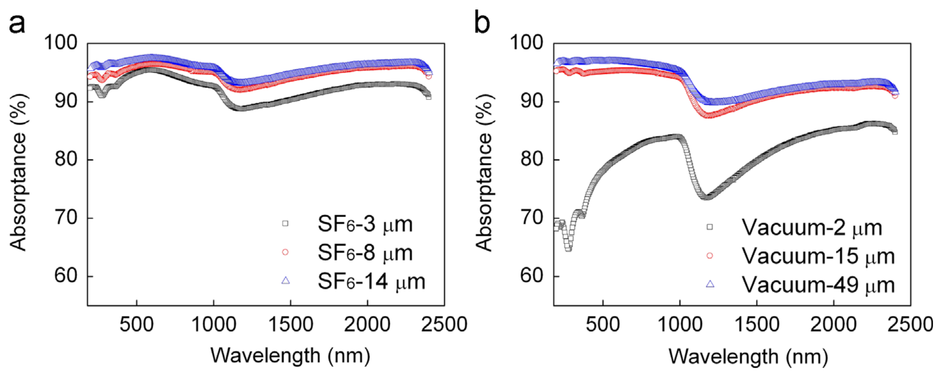

Fig. 10. The absorptance of microstructured silicon with different spike heights in the case of (a) SF_6 and (b) vacuum. The corresponding average spike heights are labeled on the graphs.

of samples fabricated in vacuum and SF_6. The measurements were performed by the UV/vis/NIR spectrometer (Lambda 1050, Perkin-Elmer) equipped with an integral spherical detector that integrates all transmitted or reflected light. The absorptance (A) of samples is determined by the equation $A=1-R-T$, where T is the transmittance and R is the reflectance. The corresponding results are shown in Fig. 10. It can be seen that when the average height of spikes fabricated in SF_6 and vacuum are close to each other, the absorptance of samples in the case of SF_6 is much higher than that of vacuum. This is caused by the additional absorption contribution from sulfur impurity. However, when the average height of spikes fabricated in the vacuum is much higher than that of SF_6 (49 VS 14 μm), the absorptance of sample fabricated in vacuum can also reach $>90\%$ in the range of 200–2500 nm. This result is beneficial for solving many key problems caused by the change of defect type that sulfur forms under high temperatures annealing process, including: the decreases of infrared absorption ability and photo-excited carriers. Therefore, these results have important implications for the later fabrication of many photoelectric devices, such as infrared sensor.

4. Conclusion

We experimentally investigate each specific relation between spike height of microstructured silicon and the fabrication parameters, including single pulse energy, pulse number, proportional relation between single pulse energy and pulse number under the same laser fluence, and ambient gas. These results prove that the fabrication of spikes with high average height can be obtained by choosing appropriate parameters. Based on these microstructures with high spike height, the surface structure of many photoelectric materials can be optimized for improving the capacity of antireflection, enhancing the infrared absorption contributed by the impurities doped in the silicon substrate, and avoiding the problems caused by sulfur impurities contained in the microstructures. These results are meaningful for the material fabrication for the solar cell, sensors, photoelectron devices, and interrelated interdisciplinary subjects.

Acknowledgments

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