J Mater Sci: Mater Electron (2016) 27:9002–9007
DOI 10.1007/s10854-016-4932-4

Near-infrared absorption enhancement in microstructured silicon by Ag film deposition

Yanchao Wang[1] · Jinsong Gao[1,2] · Haigui Yang[2] · Xiaoyi Wang[2]

Received: 13 January 2016 / Accepted: 2 May 2016 / Published online: 7 May 2016

Abstract We investigate the influence of spike-like microstructures formed on the silicon surface via fs-laser scanning with different-size on its near-infrared absorption from 1200 to 2500 nm. Although the infrared absorption of the small size microstructures is obviously lower than the large size, it can be further improved to 90 % by a large amount of random and irregular Ag nano particles from a subsequent deposition of Ag thin film. The origins of absorption enhancement are discussed and theoretically analyzed in detail.

1 Introduction

Among optoelectronic semiconductor materials, silicon (Si) is the most widely used for photodetectors and solar cells because it has the most economical price, the highest crystal quality and the most sophisticated mainstream device-fabrication processes. However, its high refractive index and a wide band gap (1.12 eV) lead to a high reflection and thus low absorption for long wavelength light. Therefore, its optoelectronic applications are limited to the visible and near-infrared spectral range which is less than 1100 nm. Recently, enhancing Si absorption in the longer wavelength range has become a topic of great interest because it has the potential to extend Si photo response into the near-infrared spectral range and therefore revolutionizes silicon-based optoelectronics through the standard silicon processing [1–7].

It is well known that pulsed laser processing can create novel materials with ultrahigh dopant concentration and tunable surface textures, which will enhance light absorption. Fs-laser processing, several groups have reported the enhancement of near-infrared absorption in Si substrate [8–12]. Although fs-laser processing can greatly enhance the infrared absorptance from 1200 to 2500 nm to the value higher than 90 % at a high laser fluence (energy per unit area), simultaneously it leads to a large-size surface microstructure more than 10 μm and therefore seriously roughens Si surface [8–11], which may cause much inconvenience for the subsequent fabrication of photoelectric devices. For example, Carey et al. [2] fabricated an infrared Si photodiode, in which only the surface microstructure with a small size (2–3 μm tall and spaced by 2–3 μm) formed at low laser fluence was adopted. Hu et al. [5] also reported an infrared Si photodiode, which had a surface with a very small microstructure size. However, for Si substrate with a small-size surface microstructure formed at low laser fluence, the enhancement of infrared absorption is limited, which is unfavorable to improve Si-based infrared response. Therefore, Si substrate with a small-size surface microstructure as well as a high infrared absorption is desired.

In this study, we show the enhancement of near-infrared light absorption in Si substrate by fs-laser irradiation. The impact of microstructure size formed at different laser fluence on infrared absorption is given. By a subsequent deposition of Ag thin films which brings in random and irregular Ag nano particles, large enhancement of infrared absorption is achieved even on a small-size surface

✉ Haigui Yang
yanghg@ciomp.ac.cn

1 University of the Chinese Academy of Sciences, Beijing 100039, China

2 Key Laboratory of Optical System Advanced Manufacturing Technology, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

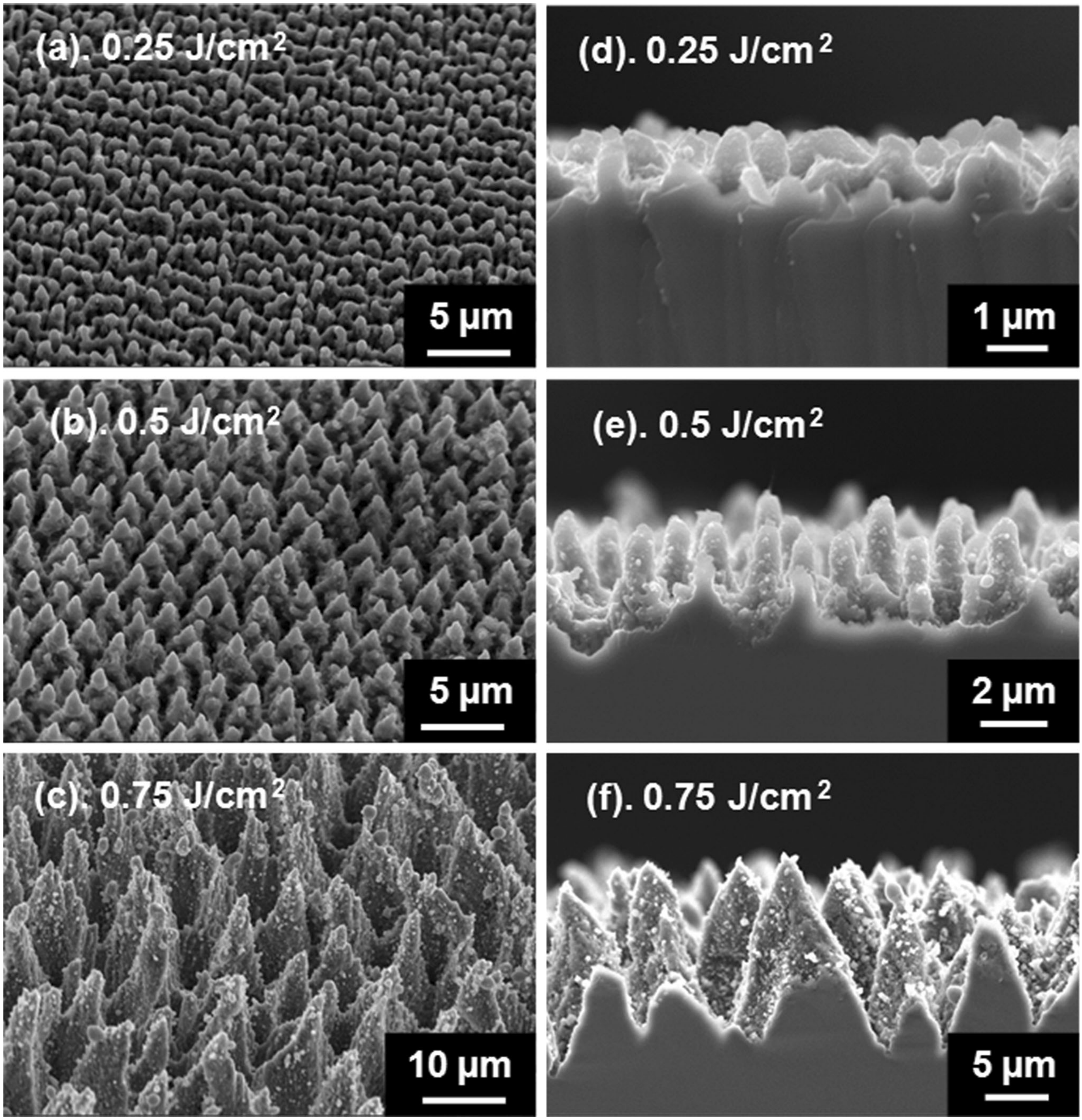

Fig. 1 Top view at a 45° angle and cross-sectional SEM images of microstructured Si by fs-laser irradiation at various fluence

microstructure. The origins of absorption enhancement are discussed and theoretically analyzed in detail.

2 Experimental details

A 450 μm thick single-side polished n-doped (100) Si wafer with a resistivity of 10 Ω cm was used as a substrate. To fabricate a microstructure surface, the cleaned Si wafer was first placed on a translation stage in a vacuum chamber evacuated to less than 1×10^{-3} Pa. Then the chamber was filled with high pure SF_6 gas at a pressure of 5×10^4 Pa. After that, the sample was irradiated in SF_6 ambient by a 1 kHz, 100 fs and 800 nm Ti: sapphire laser with various fluence. The laser spot was focused on the sample surface with a size of 150 μm in diameter. During laser irradiation, the sample was snake-scanned with a constant speed. Moreover, in order to improve light absorption, 20 nm-

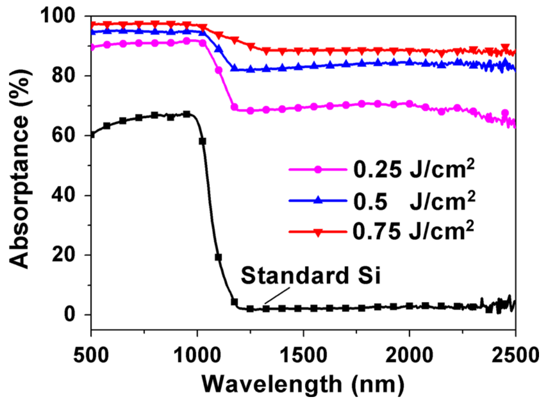

Fig. 2 The absorption spectra of microstructured Si by fs-laser irradiation at various fluence

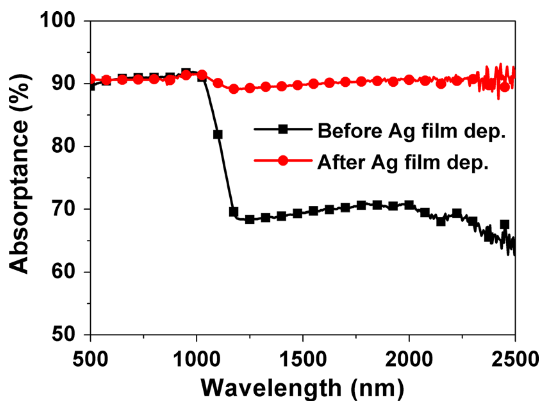

Fig. 3 A comparison of near-infrared absorption before and after 20 nm-thick Ag film deposition

thick Ag films are deposited on the microstructural surface by thermal evaporation at a rate of 0.5 Å/s. The surface morphology was characterized by a scanning electron microscope (SEM). The integrated reflectance (R) and transmittance (T) spectra between 500 and 2500 nm were measured in a Lambda-1050 spectrometer (PerkinElmer) equipped with a 160 mm integrating sphere, from which the integrated absorptance (A) spectra was extracted through A = 1–R–T.

3 Results and discussions

Figure 1 shows both the top view at a 45° angle and cross-sectional SEM images of microstructured Si by fs-laser irradiation at various fluence. It can be seen from Fig. 1a, d that Si surface exhibits an array of small size and high density microstructures fabricated by low laser fluence of 0.25 J/cm^2. The microstructure height is approximately 1.5 μm. With an increase in laser fluence, the morphology of microarray becomes sharp and large but its density decreases as shown in Fig. 1b, e. Its profile looks like a conical spike. When the laser fluence increases to 0.75 J/cm^2, the microstructure height reaches more than 10 μm. This indicates that fs-laser irradiation is a very effective method to fabricate surface microstructure on Si. The formation of surface microstructures in Fig. 1 can be attributed to two main factors. One is the well-known ultrafast plasma ablation induced by high intensity fs-laser, by which the surface Si could be ablated. Another is the assistance of SF_6 gas [8, 9]. During laser processing, high intensity fs-laser dissociates Si and SF_6 ambient gas. The dissociated SF_6 gas can etch Si by chemical reaction and consequently promotes the microstructure formation.

Figure 2 shows the absorption spectra of microstructured Si by fs-laser irradiation at various fluence, in which the standard single-side polished Si without any laser treatment is also given. Here we should pay attention to the change of infrared absorption from 1200 to 2500 nm. In this region the absorptance of standard Si is close to zero

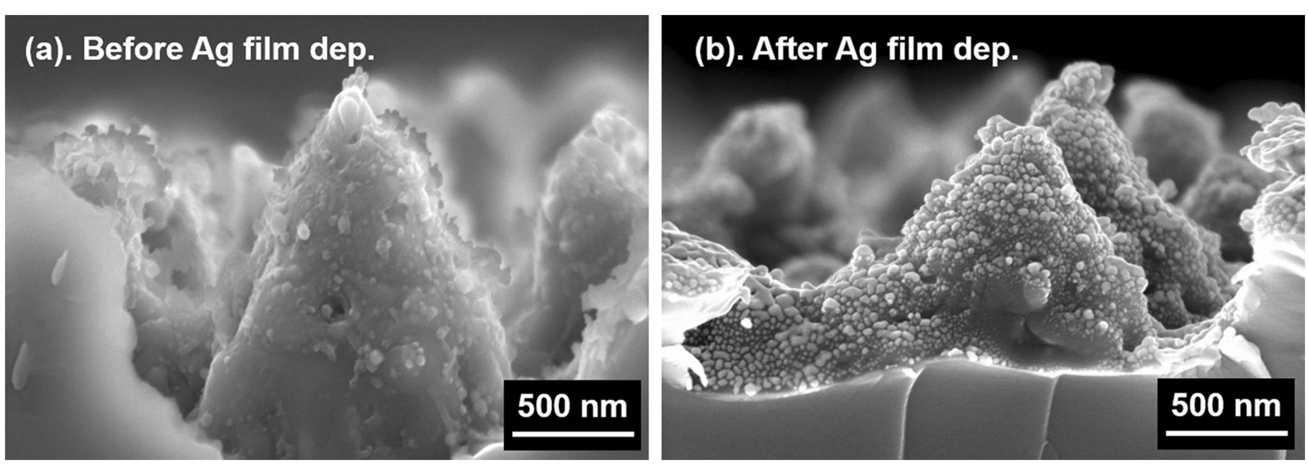

Fig. 4 High-resolution cross-sectional SEM images of microstructure surface before and after 20 nm-thick Ag film deposition

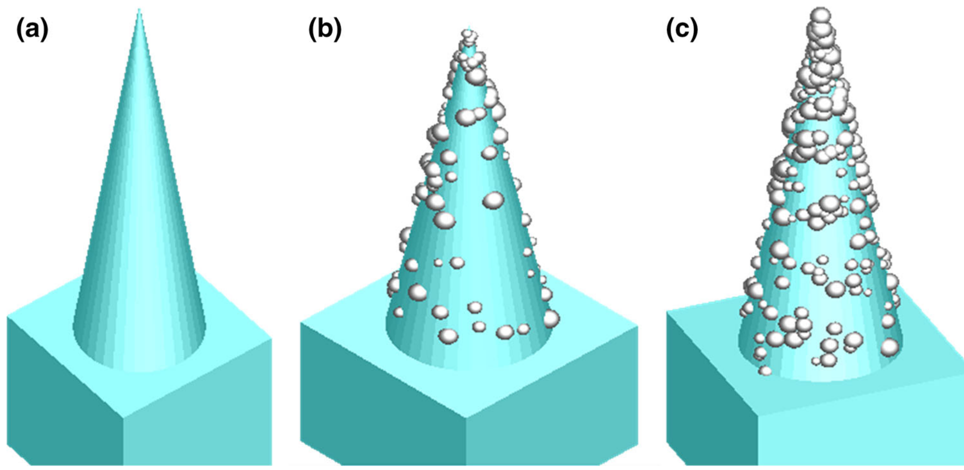

Fig. 5 The theoretical models of Si microstructure, **a** without Ag particles, and with random Ag nano particles with the total number of **b** 100 and **c** 300

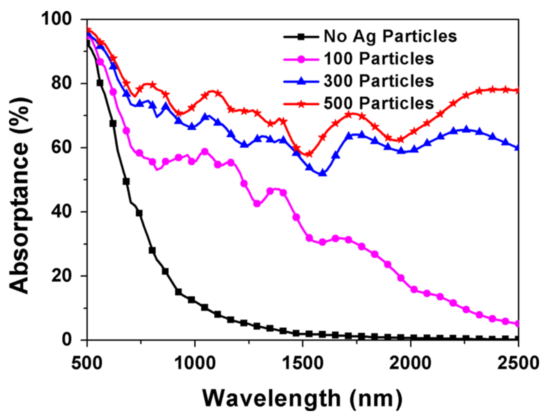

Fig. 6 The calculated absorptance without and with Ag nano particles

because of its large band gap of 1.12 eV. However, it can be seen from Fig. 2 that the absorptance is significantly enhanced after laser processing. Its value is close to 65 % at a low laser fluence of 0.25 J/cm^2. With further increase in laser fluence, the absorptance is close to 90 %. It is known that surface microstructure can enhance material absorption by reducing surface reflection. High refractive index of polished Si induces the surface reflectivity higher than 40 % (not shown) in the infrared region from 1200 to 2500 nm. However, it is found that surface infrared reflectivity reduced to the values lower than 20, 12 and 8 % at the laser fluence of 0.25, 0.5 and 0.75 J/cm^2, respectively (not shown). This indicates that the surface microstructure formed by laser processing reduces surface reflectivity. As a result, the probability that infrared photon is absorbed increases. Moreover, the increased absorptance is attributed to the natural linear absorption of Si enhanced by multiple reflections on the textured microstructure surface.

Besides above-mentioned factors, another main contribution to large enhancement of infrared absorption should be sulfur hyperdoping induced by fs-laser irradiation in SF_6 ambient. The hyperdoping layer with a thickness of more than 100 nm locates on the microstructure surface, and the doping concentration can be up to 10^{20} cm^{-3} [8], much higher than the equilibrium solubility limit. In this case theoretical studies of hyperdoping energy-band structures proved that intermediate bands near the conductance band gap were introduced into the Si band gap [13], resulting in a below-band gap absorption. That is why the infrared absorption from 1200 to 2500 nm was greatly enhanced after fs-laser irradiation.

Although high infrared absorptance of approximately 90 % in Fig. 2 could be achieved at a laser fluence higher than 0.5 J/cm^2, the surface is greatly roughened. In order to obtain a relatively low-roughness surface as well as high infrared absorption, we deposit thin Ag films with a thickness of 20 nm on the microstructure surface formed at 0.25 J/cm^2 fluence. Figure 3 shows a comparison of infrared absorption without and with Ag films. Obviously, the whole infrared absorption is further enhanced greatly after Ag thin film deposition. The average absorptance from 1200 to 2500 nm is as high as 90 %, and increased by 20 % compared with that without Ag nano particles.

Figure 4 shows the high-resolution cross-sectional SEM images of microstructure surface without and with 20 nm thick Ag films. By a comparison, it is clear from Fig. 4b that a large amount of random irregular Ag nano particles with different sizes form on the microstructure surface after the deposition of Ag thin film. The formation of Ag nano particles should be attributed to the microstructure morphology in Fig. 4a induced by fs-laser processing, on which many nanostructures are also observed. According to film growth process, during Ag thin film deposition, Ag atoms are preferentially deposited on the hills due to the shadowing effect [14]. Therefore, a large amount of random irregular Ag nano particles are formed.

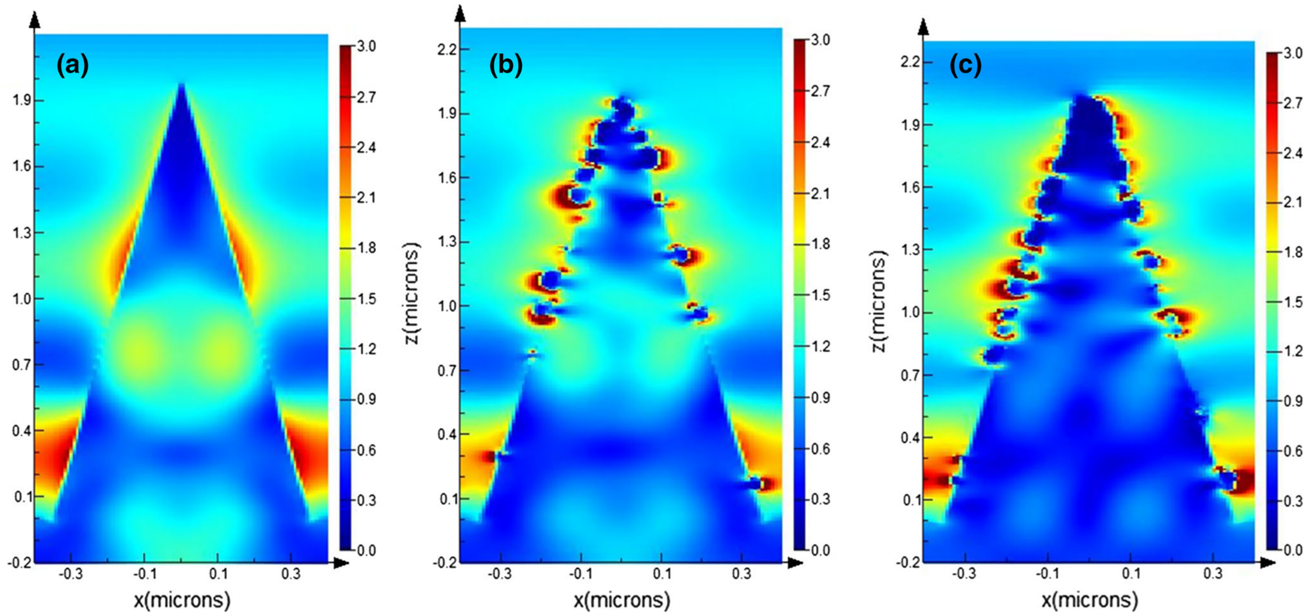

Fig. 7 A comparison of simulated electric field distribution for the wavelength of 1500 nm of Si microstructure, **a** without Ag particles, and with random Ag nano particles with the total number, **b** 100 and **c** 300

Metal nano particles usually lead to an absorption enhancement in a small range of wavelength via surface plasmon resonance. However, in this study the absorption in a very wide region is greatly enhanced by Ag nano particles. To clarify its mechanism, we theoretically simulated the effect of Ag nano particles on infrared absorption by a three-dimension finite-difference time-domain (FDTD) method. In the theoretical models of Fig. 5, the height and top angle of conical spike shown in Fig. 5a are 2 μm and 20°, which is close to the real microstructure size shown in Fig. 1a, d. Ag nano particles with diameters from 20 to 50 nm are randomly distributed onto the microstructure surface. The total number of Ag nano particles is set to 100 in Fig. 5b and 300 in Fig. 5c, respectively. The size and total number of Ag nano particles are determined by the high-resolution cross-sectional SEM images in Fig. 4, from which it can be confirmed that the size is around several ten nanometers and total number is several hundreds, respectively. Additionally, the total numbers is also determined by a theoretical model building because we find an amount of Ag particles randomly are distributed on the spike microstructure surface will overlap seriously with each other when its total number increases to 1000.

Figure 6 shows the calculated absorptance without and with Ag particles, which confirms that infrared absorption in a wide region is significantly enhanced by random and irregular Ag nano particles (100). In particular, as the number of Ag particles increases to 300, the absorption enhancement for the longer wavelength region becomes more apparent. Further increasing the number of Ag particles to 500 has no obvious effect on the near-infrared absorption. Figure 7 shows the simulated electric field distribution at a cross sectional direction for the wavelength of 1500 nm. By comparison of the electric field without and with Ag particles, it is clear that the hot spots of electric field distribute around Ag nano particles. This phenomenon is also observed for other wavelength from 1200 to 2500 nm (not shown). The strong enhancement of local electrical field intensity is due to the local excitation of surface plasmon resonance, which is induced by the incident light at the interface of Ag particle/Si. Furthermore, with the increasing of Ag particle number, by a comparison of Fig. 7b, c, the local electrical field intensity becomes stronger, especially on the tip position of microstructures. This should originate from the fact that more and more Ag particles tend to gather especially on the tip position of microstructures, as shown in Fig. 5. It was consistent with the viewpoint reported by Ref. [15, 16], when metal particles gathered or metal particles became irregular, resonance absorption band will be broadened.

By comparison of Figs. 3 and 6, it can be found that the theoretical absorptance is obviously lower than the experimental, especially for that without Ag nano particles. This difference originates from the fact that we ignore the influence of S hyperdoping on infrared absorption in the simulation because it is difficult to extract the optical constants of Si microstructure with S hyperdoping exactly. Although some difference exist between the theoretical and experimental results, large enhancement of near-infrared absorption via Ag film deposition is well explained by surface plasmon resonance effect.

4 Conclusions

By using fs-laser processing and subsequent Ag film deposition, we successfully achieved relatively low surface roughness as well as large enhancement of near-infrared absorption on microstructured Si substrate. We find that an amount of random and irregular Ag nano particls are covered onto the microstructure surface after Ag film deposition due to the shadowing effect. Our theoretical simulation reveals that surface plasmon resonance induced by random and irregular Ag nano particles is the further-enhancement origin of near-infrared absorption in a wide region.

Acknowledgments Project supported by the National Natural Science Foundation of China (Nos. 61306125 & U1435210), the Science and Technology Innovation Project (Y3CX1SS143) of CIOMP, the Science and Technology Innovation Project of Jilin Province (Nos. Y3293UM130 & 20130522147JH & 20140101176JC).

References

1. E. García-Hemme, R. García-Hernansanz, J. Olea, D. Pastor, A.D. Prado, I. Mártil, G. González-Díaz, Room-temperature operation of a titanium supersaturated silicon-based infrared Photodetector. Appl. Phys. Lett. **104**, 211105 (2014)
2. J.E. Carey, C.H. Crouch, M. Shen, E. Mazur, Visible and near-infrared responsivity of femtosecond-laser microstructured silicon photodiodes. Opt. Lett. **30**, 1773–1775 (2005)
3. J. Yang, F. Luo, T.S. Kao, X. Li, G.W. Ho, J. Teng, X. Luo, M. Hong, Design and fabrication of broadband ultralow reflectivity black Si surfaces by laser micro/nanoprocessing. Light Sci. Appl. **3**, 66 (2014)
4. B. Fazio, P. Artoni, M.A. Iatì, C. D’Andrea, M.J.L. Faro, S.D. Sorbo, S. Pirotta, P.G. Gucciardi, P. Musumeci, C.S. Vasi, R. Saija, M. Galli, F. Priolo, A. Irrera, Strongly enhanced light trapping in a two-dimensional silicon nanowire random fractal array. Light Sci. Appl. **5**, 62 (2016)
5. S. Hu, P. Han, S. Wang, X. Mao, X. Li, L. Gao, Improved photoresponse characteristics in Se-doped Si photodiodes fabricated using picosecond pulsed laser mixing. Semicond. Sci. Technol. **27**, 102002 (2012)
6. M.A. Green, Thin-film solar cells: review of materials, technologies and commercial status. J. Mater. Sci. Mater. Electron. **18**, S15–S19 (2007)
7. Z. Ouyang, S. Pillai, F. Beck, O. Kunz, S. Varlamov, K.R. Catchpole, P. Campbell, M.A. Green, Effective light trapping in polycrystalline silicon thin-film solar cells by means of rear localized surface plasmons. Appl. Phys. Lett. **99**, 261109 (2010)
8. Y. Liu, S. Liu, Y. Wang, G. Feng, J. Zhu, L. Zhao, Broad band enhanced infrared light absorption of a femtosecond laser microstructured silicon. Laser Phys. **18**, 1148–1152 (2008)
9. M.A. Sheehy, B.R. Tull, C.M. Friend, E. Mazur, Chalcogen doping of silicon via intense femtosecond-laser irradiation. Mater. Sci. Eng. B Adv. **137**, 289–294 (2007)
10. Y. Peng, X. Chen, Y. Zhou, G. Xu, G. Xu, B. Cai, Y. Zhu, J. Xu, R. Henderson, J. Dai, Annealing-insensitive “black silicon” with high infrared absorption. J. Appl. Phys. **116**, 073102 (2014)
11. Y. Peng, Y. Zhou, X. Chen, Y. Zhu, The fabrication and characteristic investigation of microstructured silicon with different spike heights. Opt. Commun. **334**, 122–128 (2015)
12. X. Dong, N. Li, Z. Zhu, H. Shao, X. Rong, C. Liang, H. Sun, G. Feng, L. Zhao, J. Zhuang, A nitrogen-hyperdoped silicon material formed by femtosecond laser irradiation. Appl. Phys. Lett. **104**, 091907 (2014)
13. H. Shao, C. Liang, Z. Zhu, B.Y. Ning, X. Dong, X.J. Ning, L. Zhao, J. Zhuang, Hybrid functional studies on impurity-concentration-controlled band engineering of chalcogen-hyperdoped silicon. Appl. Phys. Express **6**, 133–142 (2013)
14. T. Karabacak, Thin-film growth dynamics with shadowing and re-emission effects. J. Nanophotonics **5**, 052501 (2011)
15. H. Mutschke, A.C. Andersen, D. Clément, T. Henning, G. Peiter, Infrared properties of SiC particles. Astron. Astrophys. **345**, 187–202 (1999)
16. P. Zhang, S. Li, C. Liu, X. Wei, Z. Wu, Y. Jiang, Z. Chen, Near-infrared optical absorption enhanced in black silicon via Ag nanoparticle-induced localized surface plasmon. Nanoscale Res. Lett. **9**, 519 (2014)