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EPL, 110 (2015) 68005

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Quantification of absorption contributions in microstructured silicon fabricated by femtosecond laser pulses

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received 14 April 2015; accepted in final form 22 June 2015
published online 13 July 2015

PACS 81.40.-z – Treatment of materials and its effects on microstructure, nanostructure,
and properties

PACS 42.25.Bs – Wave propagation, transmission and absorption

Abstract – Microstructured silicon material, fabricated by femtosecond laser pulses, has a lot of crucial applications in silicon-based photovoltaics, photo-detectors, and super-hydrophobic devices etc., due mainly to the high absorption in both visible and infrared regions. However, the mechanisms attributed to its high-absorption characteristics have never been accurately quantified, which limits further the exploitation of this kind of material. Here, we experimentally quantify different absorption contributions in microstructured silicon fabricated by femtosecond laser pulses, which can be attributed to dopant impurities in the silicon substrate, doping impurities induced during the laser fabrication process, absorption enhancement from the light-trapping structure, and surface disordered material formed also during the laser fabrication process. From these analyses, we determine that with the assist of a light-trapping structure, dopant impurities in the silicon substrate contribute much more to the infrared absorption than those of the doping sulfur impurities induced during the fabrication process. Furthermore, the infrared absorption of material can be annealing-insensitive. These results have important implications for the design and fabrication of high-efficiency optoelectronic devices.

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Introduction. – Tapered silicon micro/nanostructures can drastically decrease the interface reflection for incident light at the air-silicon interface, but such structures do not contribute to additional infrared absorption below the silicon band gap. Since Mazur *et al.* created arrays of sharp conical structures by repeatedly irradiating silicon surfaces with femtosecond laser pulses in SF₆ ambient [1], the laser-fabricated microstructure silicon (LFMS) came along with another absorption mechanism that results from high non-equilibrium sulfur densities incorporated during structure manufacturing. Then, this kind of LFMS attracts more and more interest [2–5] for its potential applications in silicon-based photovoltaics [6–8], photo-detectors [9–11],

and super-hydrophobic devices [12,13]. It was found that the infrared absorption of this special LFMS can be attributed to many factors, including dopant impurities in the silicon substrate [14], impurities doped during laser fabrication [15,16], light-trapping structures [17], and surface disordered material [18,19]. Basing on different fabrication processes, the effect of each factor in LFMS material may be completely different. For example, LFMS is usually fabricated in sulfur-bearing gases, and then single sulfur atoms can substitute lattice positions in the bulk silicon and significantly improve the infrared absorption [20]. On the other hand, the dopant impurities (such as phosphorus) in the silicon substrate also contribute to the infrared absorption. Even though such a contribution is small, it can be accumulated to a prominent value when

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the light-trapping structure is formed on the silicon surface [14,17]. Therefore, it can be concluded that different factors in LFMS have different contributions to the infrared absorption. If each of the contributing factors can be further quantified, it would be a great benefit for the design and fabrication of high-efficiency optoelectronic devices. Hence, it is extremely important to distinguish the absorption contributions from these factors.

In this paper, we present quantitative analyses of different absorption contributions in LFMS: First, we obtain LFMS material in vacuum and in the traditional SF₆ gas ambient, and experimentally ensure that they have the similar infrared absorptance (> 90%); second, we use high-temperature annealing processes to distinguish the contributions from active sulfur impurities and surface disordered material; third, we determine the absorption contribution from the dopant impurities in the silicon substrate; and finally, by comparing these data, we can obtain a quantitative contribution of each factor to the total absorptance, which can be used to design and optimize LFMS with different fabrication methods and parameters.

Results and discussions. – We experimentally fabricate two-dimensional high-aspect-ratio microstructures on a silicon surface. The laser pulses used in the experiments are produced by a Ti:Sapphire regenerative amplifier, typically 800 nm, 1 kHz, and 130 fs. The laser beam is focused with a convex lens ($f = 1$ m), and delivered into a chamber through a quartz window of 0.4 mm thickness. The contrastive ambient atmospheres chosen here are SF₆ and vacuum. In order to avoid the effect of residual impurities from the ambient gas, two separate chambers are used for the microstructures fabrication, one for the SF₆ atmosphere and the other for vacuum. The pressure in the vacuum chamber is kept at $\sim 1 \times 10^{-4}$ torr constantly, while for the chamber with SF₆, the base pressure is $\sim 1 \times 10^{-4}$ torr and then fills back with SF₆ to a pressure of 500 torr. The chambers are mounted on motor-driven translation stages to allow two-dimensional microstructures area. The silicon wafer (phosphorus-doped n-type silicon wafer, resistivity: 0.01–0.02 $\Omega \cdot \text{cm}$) is mounted in the vacuum chamber with the (100) face placed vertically, and directed toward the incident laser beam. The laser spot on the sample surface is monitored by a CCD beam profiler and the diameter of each spot is set to about 300 μm by adjusting the distance between the silicon wafer and the laser focal point. Furthermore, a quarter-wave plate (or half-wave plate) and polarizing beam splitter are used to adjust the intensity of the incident laser beam. A beam shutter is used to control the pulse number. The absorptance measurements are performed by an UV/Vis/NIR spectrometer (Lambda 1050, PerkinElmer) equipped with an integral spherical detector that integrates all transmitted or reflected light. The sample absorptance (A) is determined by the equation $A = 1 - R - T$, where T is the transmittance and R is the reflectance. In order to process a sufficiently large area for spectroscopic

measurements of optical reflectance and transmittance, two-dimensional laser-structured areas are fabricated on the silicon surface by scanning a straight line (width a , horizontal orientation) at a speed-velocity V , with a D shift (vertical orientation) between two adjacent parallel scans to treat the whole surface. According to the equation $N = a^2 f / (VD)$ [21], the number of shots (N) received anywhere on the sample surface (except on the edges) is 1000 (in our experiments, $a = 300 \mu\text{m}$, with laser repetition $f = 1$ kHz, $V = 1200 \mu\text{m/s}$, and $D = 75 \mu\text{m}$).

Before analyses, all absorption factors in LFMS should be clarified. First, the absorption resulting from impurities in the silicon substrate is considered. The single-crystal silicon wafer used in our experiments is a low-impedance sample (0.01–0.02 $\Omega \cdot \text{cm}$, with corresponding phosphorus dopant density $\sim 10^{18} \text{cm}^{-3}$), where the phosphorus impurities can contribute to the infrared absorption. Second, there is formation of new doping levels caused by impurity doping during the laser fabrication process. An impurity, such as sulfur, can be embedded into the microstructure surface layer during the interaction process among laser, SF₆ gas, and silicon material, and then promoting light absorptance [18]. Third, we take into account the enhanced phosphorus absorption caused by the light-trapping structure. The difference in absorptance between spiked and flat materials is due primarily to multiple reflections off the rough surface of the spiked material. The light-trapping structure itself does not create or imply any absorption mechanism, but each reflection provides another opportunity for part of the incident/reflected light to be refracted into the material and absorbed by the phosphorus impurities. When these small absorption contributions are accumulated over many reflections, the overall infrared absorption can be greatly improved. Finally, during the process of structuring, a layer of disordered material (which contains silicon nanocrystallites, nanopores, and impurities) is formed and covers the surfaces of spikes, which can also contribute to a certain sub-band gap absorption [18,22]. Therefore, for the LFMS obtained in vacuum, there are three factors contributed to the total absorptance: phosphorus impurity states, light-trapping structure and disordered material. While in the case of SF₆, there are four factors: phosphorus impurity states, sulfur impurity states, light-trapping structure, and disordered material.

To clearly quantify these absorption contributions in LFMS, it is necessary to produce samples with similar values of absorptance before subjecting them to any processing. Therefore, the average height of spikes are optimized under the condition of vacuum and SF₆ by using different laser energies [23,24]: *i.e.*, the average height of spikes is higher in the case of vacuum in order to realize a similar light absorptance (> 90%) as those samples fabricated in the SF₆ gas ambient. The typical dimensions of these fabricated spikes are as follows: average heights are about 56 and 14 μm for the case of vacuum and SF₆, respectively; the corresponding base diameters are about 25 and 8 μm ,

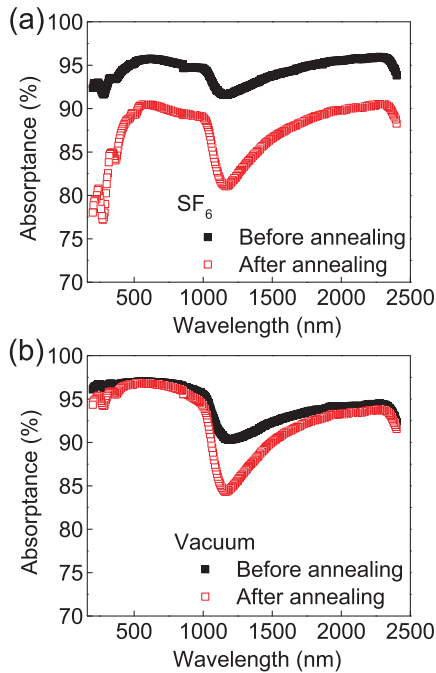


Fig. 1: (Colour on-line) The absorbance of microstructured silicon fabricated in the ambient of (a) SF_6 , (b) vacuum before and after annealing. The annealing temperature is 1000°C .

respectively. The corresponding absorption results are shown in fig. 1 (solid rectangles). The absorbance of both the SF_6 - and vacuum-fabricated samples remains above 90% across the spectral range being studied, and the absorbance values of the two samples stay within 5% difference from each other at all wavelengths. Therefore, these absorption-unified samples can be used for the later testing.

Samples are then furnace annealed in an atmosphere of flowing argon for 5 min at 1000°C . The temperature change rate is 100°C/s (AccuThermo AW610, Rapid Thermal Process System). As the SEM pictures show in fig. 2, the surface morphology of microstructures in both cases does not have obvious changes. While under this annealing conditions, the surface disordered material is significantly recrystallized to crystalline silicon [18], and the function of sulfur impurities for the infrared absorption can be completely removed (the average concentration of sulfur impurities in the microstructure region is about $3 \times 10^{20} \text{ cm}^{-3}$ [14,25]). Therefore, as presented by open rectangles in fig. 1, the absorbance of SF_6 samples decreases markedly, while the absorbance of the vacuum samples experiences little change except for a small wavelength range around 1100 nm.

The absorption decrease around 1100 nm observed in both samples is theorized to be caused by the crystallization change in the microstructures during the annealing process. The energy gap of single-crystal silicon is 1.1 eV; therefore, only incident photons with wavelengths below 1100 nm can be effectively absorbed to create free

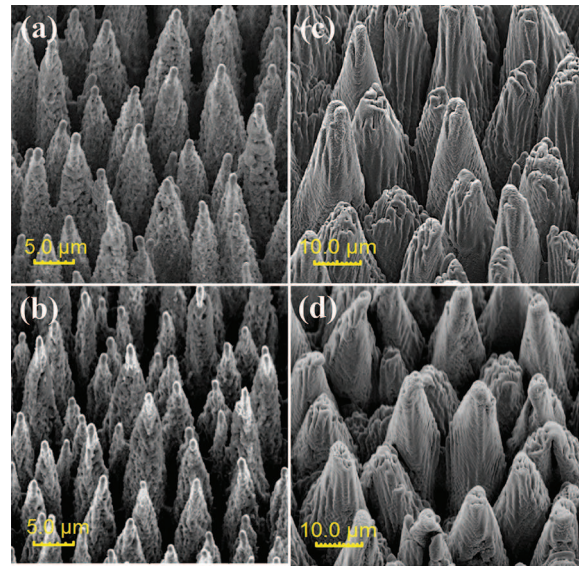


Fig. 2: (Colour on-line) SEM images of microstructured silicon fabricated in the ambient of (a), (b) SF_6 and (c), (d) vacuum: (a), (c) before annealing; (b), (d) after a 1000°C annealing process.

carriers. When microstructures are formed on the silicon surface, the light-trapping structure enhances the infrared absorption with the help of phosphorus impurities. In addition, a layer of disordered material is also formed and covers the surfaces of spikes. The disordered material contains silicon nanocrystallites, nanopores, and impurities, which can increase the multiple reflection of light and then promote the absorption of impurities for light. Under high-temperature annealing, the disordered material is recrystallized, but even complete recrystallization cannot eliminate the below-band gap absorption of material completely [18]. Therefore, absorption of the region around 1100 nm drops after annealing but not as low as the original substrate silicon.

In the case of vacuum, the absorption contribution of disordered material can be calculated from the difference of absorbance before and after annealing, which is related to the wavelength. While in the case of SF_6 , the absorbance difference caused by annealing includes two parts: sulfur impurities and disordered material. Considering that the ingredient of disordered material is basically the same after the annealing process, and the disordered material is only covered on the surfaces of spikes, therefore, the absorption contribution of disordered material in the case of SF_6 can be calculated according to the height ratio of spikes in two cases. After that, the absorption contribution of sulfur impurities as a function of wavelength can be calculated.

Combining the accumulated data provided above and the absorbance of single-crystal silicon, the absorption enhanced by light-trapping structure can be deduced. Here, we need to emphasize that the light-trapping structure itself does not absorb light, it just provides more chances

Table 1: Absorptance originated from different factors. Data represent an annealing temperature of 1000 °C. The standard deviations (statistic over 5 samples) are also presented.

Absorptance	SF ₆ (%)	Standard Deviation (%)	Vacuum (%)	Standard Deviation (%)
A	96	0.12	93	0.04
A_{dm}	$(14/56) \times 1 = 0.25$	0.02	$93 - 92 = 1$	0.04
A_{s}	$(96 - 90 - 0.25) = 5.75$	0.14	0	0
A_{ps}	65	0.01	65	0.01
A_{pLT}	$(90 - 65) = 25$	0.13	$(92 - 65) = 27$	0.05

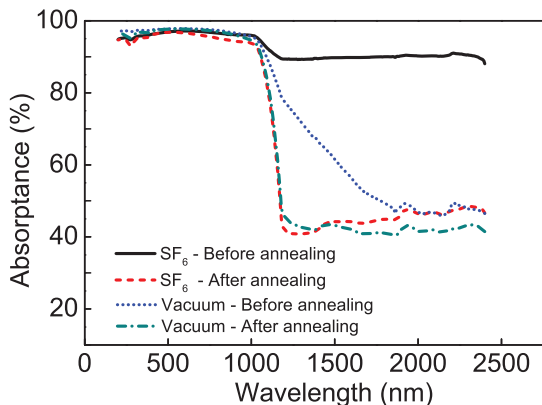


Fig. 3: (Colour on-line) The absorbance of LFMS obtained by using high-impedance silicon (resistivity: 20000–28000 $\Omega \cdot \text{cm}$).

for the light to be absorbed by the phosphorus impurities. Therefore, if there are negligible phosphorous impurities in the silicon substrate, the absorbance of LFMS after annealing should be the same in two cases. In order to verify this, we repeat our experiments above by using the high-impedance silicon (resistivity: 20000–28000 $\Omega \cdot \text{cm}$), the corresponding results are shown in fig. 3. It can be clearly seen that the LFMS in the case of vacuum does not have the high absorbance as that of the SF₆ case, and, after annealing, the absorbance curves in two cases are almost overlapped with each other. Comparing with fig. 1, we can understand better that the contribution of the light-trapping structure can only be realized when it is combined with the phosphorus impurities in the silicon substrate or the doping impurities during the fabrication process.

An expression can be used to consider all absorption contribution factors in LFMS:

$$A = A_{\text{ps}} + A_{\text{s}} + A_{\text{dm}} + A_{\text{pLT}}, \quad (1)$$

where A is the total absorbance, A_{ps} , A_{s} , A_{dm} , A_{pLT} are the absorbance contributed from phosphorus impurities in the substrate, sulfur impurities, surface disordered material, and phosphorus impurities in the light-trapping structure, respectively. A_{ps} can be obtained from the absorption curve of single-crystal silicon [17], in which the absorption of phosphorus impurities from the substrate is also enhanced greatly by the multiple reflections between two surfaces of the single-crystal silicon; A_{dm} can

be obtained from the difference of absorbance before and after annealing in the case of vacuum; A_{s} can be obtained by combining A_{dm} and the difference of absorbance before and after annealing in the case of SF₆; A_{pLT} can be obtained from the difference between A_{ps} and the absorbance after annealing. We take the wavelength of 2000 nm for an example, the relative absorption contributions from each factor are shown in table 1 for both the vacuum and SF₆ samples.

In the case of SF₆, proportions are determined to be $A_{\text{dm}} : A_{\text{s}} : A_{\text{pLT}} : A_{\text{ps}} = 0.25 : 5.75 : 25 : 65$, while in the case of vacuum, the values are found to be $A_{\text{dm}} : A_{\text{s}} : A_{\text{pLT}} : A_{\text{ps}} = 1 : 0 : 27 : 65$. It is evident that in the absence of the sulfur impurities, a high absorbance can still be realized by combining the light-trapping structure and the phosphorus-doped low-impedance silicon substrate, and this process can avoid the detrimental effect on photocurrent attributed by inactive sulfur impurity states. Furthermore, basing on the accumulated data for each of the contributing factors affecting absorption, this would greatly assist the research in the microstructure silicon field and benefit the application in the process of optoelectronic devices fabrication, which is not limited to those processed in SF₆ or vacuum. Therefore, this quantitative analysis provides us another effective guidance to realize superior properties for optoelectronic devices.

Conclusion. – In summary, we have quantified different absorption contributions in LFMS, including dopant impurities (phosphorus) in the substrate, doping impurities (sulfur) during the fabrication process, absorption enhanced by light-trapping structures, and surface disordered material, over the spectral range from 200 to 2500 nm. Detailed analyses have been carried out, indicating that the absorption contributions from the combination of phosphorus impurities in the substrate and light-trapping structure play dominant roles. These results provide significant guidelines for the design and fabrication of high-efficiency semiconductor devices.

This work is partly supported by Program of Shanghai Subject Chief Scientist (14XD1403000), Shanghai Basic Research Key Project (14DZ1206600, 12JC1407100, 13231203100), “Chen Guang” Project of Shanghai Municipal Education Commission and Educational

Development Foundation (12CG54), State Scholarship Fund (201308310172), and New Century Excellent Talents from Ministry of Education (NCET-12-1052).

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