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Full Length Article

Study on top sulfur hyperdoping layer covering microstructured Si by fs-laser irradiation

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ABSTRACT

We studied the infrared absorption of a top sulfur hyperdoping layer covering an fs-laser irradiated microstructured Si substrate. To clarify the hyperdoping concentration distributions, and to find out how the top hyperdoping layer affects infrared absorption from 1200 to 2000 nm, a continuous etching treatment was utilized. Then we interpreted the thermal stabilization of both infrared absorption and sulfur hyperdoping concentration. The fundamental cause for infrared-absorption degradation under thermal annealing was explained. Furthermore, we discussed in detail how the interaction between the top hyperdoping layer and surface microstructure contributed to the high infrared absorption by a series of theoretical simulations using a finite-difference time-domain method. A strong localization of an incident electromagnetic wave was observed around the top sulfur hyperdoping layer covering microstructured Si, which played a critical role in improving infrared absorption. The results in this paper are especially beneficial to the subsequent fabrication of photoelectric devices and infrared response improvement.

1. Introduction

Developing low-cost infrared imaging systems or sensors is of great interest for wide applications in the telecommunications, security, and automotive industries. Silicon (Si), as the second-most-abundant element in the Earth's crust, satisfies the low-cost and on-chip complementary metal-oxide semiconductor (CMOS) compatibility criteria. However, its wide intrinsic band gap of 1.12 eV limits the infrared photoresponse of Si devices to roughly less than 1100 nm. Several attempts to extend its photoresponse limit to a longer infrared wavelength involve forming heterostructures with traditional narrow-band-gap Ge or SiGe materials [1,2], plasmonic metallic nanoantennas [3–5], and incorporating chalcogen hyperdoping in Si [6–13]. By improving infrared light absorption ability, all these approaches can result in extending the infrared response of Si-based devices, although they are based on different physical mechanisms.

A promising approach to extend the infrared photoresponse is incorporating chalcogen hyperdoping in a Si substrate [9,10]. The Chalcogen hyperdoping is able to create a dopant concentration as high as 10^{20} cm^{-3}, far beyond their solid solubility limit. In the case of the hyperdoping, electron-electron interaction couples the energy levels into a band, often referred to as an impurity or intermediate band [11,12], which extends the long-wavelength limit of infrared absorption through sub-band-gap absorption. In addition to the fabrication of the so-called laser-induced periodic surface structures which is used for optical storage and planar optoelectronic circuits, such as self-organized periodic structures [14], nanohillocks and nanoholes [15], femtosecond-laser (fs-laser) irradiation can incorporate chalcogen hyperdoping effectively. Different from ion implantation [7,8], hyperdoping via fs-laser irradiation is accompanied by surface microstructure generation due to high-intensity laser ablation. This leads to a much higher absorption (roughly above 90%) compared with that prepared by ion implantation [7,8]. The physical mechanisms of the hyperdoping-induced infrared absorption have been studied by many researchers through experiments and theoretical calculations [6–8,11–13]. However, in order to extract satisfactory infrared photoresponse in microstructured Si, clarifying the interaction between top hyperdoping layer and surface microstructure contributing infrared absorption, and achieveing a further high infrared absorption while maintaining a small surface roughness is greatly desired.

In this study, we investigated the infrared-absorption enhancement occurring in a top sulfur hyperdoping layer covering microstructured Si by fs-laser irradiation. Firstly, we clarified hyperdoping concentration distributions, and how the top hyperdoping layer affects infrared

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absorption from 1200 to 2000 nm by a continuous etching treatment. We then studied the thermal stabilization of both infrared absorption and sulfur hyperdoping concentration. Finally, we discussed in detail how the interaction between the top hyperdoping layer and surface microstructure contributes to the high infrared absorption through a series of theoretical simulations using a finite-difference time-domain method.

2. Experiment design and fabrication

In this experiment, a single-sided polished and boron-doped Si substrate wafer with a resistivity of 10 Ω cm was used to cut to a size of $2 \times 2\,cm^2$. After cleaning of organic and metallic surface contamination, the wafer was immediately placed on a translation stage in a vacuum chamber evacuated to less than 1×10^{-3} Pa. The chamber was filled with high-purity SF_6 gas at a pressure of 5×10^4 Pa. The wafer was irradiated by a 1-kHz, 100-fs, 800-nm Ti:sapphire laser with a snake-scanned route under high and low laser fluence, separately. The laser was then focused vertically on a 150-μm-diam spot on the surface of the sample by a lens with a focal length of 0.5 m. After fs-laser processing, the top hyperdoping layer of microstructured Si sample was etched by reactive ion etching (RIE) to study its optical properties. Moreover, a thermal annealing treatment was performed at 1075 K in a furnace with N_2 ambient for 30 min to study its thermal stabilization.

To analyze the absorption of microstructured Si, we measured the integrated reflectance (R) and transmittance (T) spectra between 500 and 2000 nm in a Lambda-1050 spectrometer (PerkinElmer, USA) equipped with a 160-mm integrating sphere. Then the integrated absorptance (A) spectra were extracted through A = 1–R–T. Furthermore, we characterized surface morphology of the sample using scanning electron microscopy (SEM), also sulfur hyperdoping concentration distribution using secondary-ion mass spectrometry (SIMS) and crystal properties in the surface layer using confocal Raman spectroscopy with a 632 nm laser excitation.

3. Results and discussion

A schematic drawing of the fs-laser irradiation method is shown in Fig. 1(a). And the surface microstructures illustrated in diagram of Fig. 1(b) can be formed. Fig. 1(c) shows the fabricated microstructured surface measuring $2 \times 2\,cm^2$ on the Si substrate. The integrated reflectance of the microstructured surface in the visible region is less than 5% due to the anti-reflection microstructures, and therefore the surface looks very black. Fig. 2(a) and (b) show the surface microstructure morphology from different views. After fs-laser irradiation, two typical features on the microstructured surface were observed: one is that an array of micrometer-sized conical spikes with quasi-periodic distribution was created, and the other is that there was a large amount of nanoscale particles spread across a surface of conical spikes. Since conical spikes induced by fs-laser irradiation were first observed by Mazur's group [13], the formation mechanisms and the influence of experimental conditions on surface morphology have been widely studied by many researchers [16–21]. In addition to laser parameters such as fluence and pulse duration, the ambient gas plays a critical role in the spike microstructure morphology. The surface irradiated in N_2 or vacuum ambient has even blunter microstructures [20,21]. However, the conical spikes formed in SF_6 ambient in this study exhibit much sharpness, as shown in Fig. 2(a) and (b). In SF_6 ambient, high-intensity laser pulses can ablate Si surface and simultaneously dissociate SF_6, resulting in a chemical reaction between Si and SF_6, by which the radicals etch Si via volatile SiF_4 formation. Besides that, laser pulse can also enhance the reactivity by inducing vibrationally excited SF_6 [22].

When fs-laser pulses interact with Si in SF_6 ambient, on the other hand, the ultra-fast melting and ultra-fast condensation will bind sulfur atoms generated by dissociated SF_6 to form a nonequilibrium hyperdoping layer on the Si surface. Fig. 2c presents the concentration profile of doped sulfur atoms distributed in the surface layer after fs-laser irradiation. It is determined by a SIMS method using a CAMECA 6F with a 25° incident angle and 14.5 keV Cs+ beam. The detected area is a 30 μm-diameter circle containing several tens of spikes. Therefore, these results reflect the average concentration of sulfur in conical spikes. In Fig. 2c the sulfur doped depth (thickness of top hyperdoping layer coverd on the microstructure) is defined as the depth (thickness) along the vertical direction of the lateral surface of the conical structures. The doped depth is then determined by "Depth = L × sin θ", where L is the measured longitudinal depth, and θ is half of the cone angle of the microstructure in the detected area. According to the Fig. 2(b) and (e), we set θ to 15° for both before and after etching respectively, which is half of the average angle of the microstructures in the detected area. Similar hyperdoping concentration distribution determined by SIMS method has been demonstrated by Zhuang et al [20]. From Fig. 2(c), we can see that sulfur atoms have been hyperdoped into the surface layer of the conical spikes shown in Fig. 2(a) and (b). Sulfur dopant concentration in the uppermost 200-nm depth is more than $10^{20}\,cm^{-3}$, several orders of magnitude greater than its solid solubility limit of $3 \times 10^{16}\,cm^{-3}$ in Si crystals [23–26]. Thus, fs-laser irradiation can simultaneously realize surface microstructuring and atom hyperdoping.

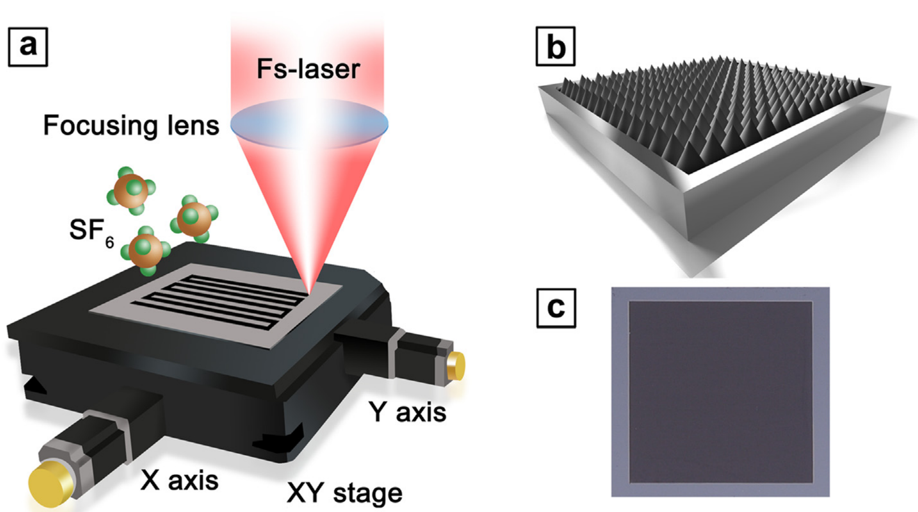

Fig. 1. (a) Schematic of fs-laser irradiation for microstructured Si fabrication. (b) Diagram of surface microstructures. (c) Photograph of fabricated microstructured Si surface.