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Absorption enhancement in nanostructured silicon fabricated by self-assembled nanosphere lithography

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In this work, we give a detailed experimental and theoretical analysis of a nano cone array on silicon wafer, which can greatly enhance the absorption compared with the polished silicon. The experimental absorptance can reach 98.7% in the wavelength ranging from 400 nm to 1100 nm. The mechanism of absorption enhancement is attributed to the nano cone array that can suppress the reflection by building a grade index from air to silicon surface. Moreover, an ultrathin 13 nm thickness gold film was sputtered on the nano cone array, by which surface plasmon can be excited and the absorption in the near-infrared region can be greatly enhanced. We also give a deep comprehending on the physics mechanism of such high absorption. This kind of nano cone array can be fabricated by a simple and low-cost colloidal sphere lithography and reactive ion etching, which makes it a more appropriate candidate for photovoltaics, spectroscopy, photodetectors, sensor, especially for the silicon-based application in the near-infrared region.

1. Introduction

It is well known that silicon (Si) is the most widely used for photodetectors [1] and solar cells [2–4] among semiconductor materials because it has many great advantages such as low cost, high performance and mature fabrication processes. Si as a kind of semiconductor material, is typically used to absorb photons and generate electron-hole pairs leading to the flow of photocurrent. However, flat silicon surface has high natural reflectance of around 30%–40% in the visible region, which degrades the efficiency of photoelectric conversion [5]. What is worse, to generate the electron-hole pairs inside a semiconductor, the energy carried by the incident electromagnetic wave should be higher than the bandgap of the semiconductor. So the large energy bandgap (1.12 ev) of Si decides silicon-based applications are mainly concentrated in the visible range (less than 1100 nm) [6]. Therefore, enhancing the absorption of Si become a topic of great interest especially in the near-infrared region, because it has the potential to extend silicon-based optoelectronic devices into the longer wavelength region (>1100 nm). Although many groups used femtosecond laser to fabricate black silicon that can also enhance the light trapping effect, increasing the optical absorption [7–9], this kind of textured surface structures produced by laser ablation are usually on micrometer scale, the size and aspect ratio of the surface structures are limited by the laser processing parameters.

In recent years, surface plasmon (SP) around metallic nanostructure provides an unprecedented way to rout and manipulate light on a nanoscale, which plays a vital role in various fields such as color filter [10–12], surface-enhanced Raman scattering (SERS) [13,14], extraordinary optical transmission (EOT) [15,16], sensor [17,18], and energy harvest [19–23]. SP is generated by coherent oscillations of free electrons coupled to an incident electromagnetic field, which is categorized into propagating surface plasmons (PSPs) and localized surface plasmons (LSPs). When the metal surface is in contact with a semiconductor forming a Schottky barrier, the SP excited by the nano metal structure can create energetic or hot electrons through nonradiative decay process, and these hot electrons can be injected into the conduction band of the neighboring semiconductor materials before thermalization resulting in photocurrent [24]. In this case, the barrier energy can

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be much lower than the bandgap of the semiconductor, and the low-energy electrons can jump more easily into the conduction, which lays the fundamental of many silicon-based hot electron devices [25–28] in the near-infrared region. Moreover, the absorption peak can be tuned in a wide range by engineering the shape and size of the nano structure in order to achieve photoelectric response in the desired wavelength region. Many previous works have been widely studied both theoretically and experimentally in a variety of structures including metal grating [25], nanoparticles [26], nano cube [27], and nano hole [28]. However, these findings usually focus on a narrowed absorption band and the fabrication of these subwavelength nanostructures usually involves in electron beam lithography (EBL), which is costly and turns out to be a challenge for the application in large area. Despite these great achievements, it is still a challenge to realize efficient absorption in silicon-based devices with wide band especially in the near-infrared, and low cost, simple fabrication simultaneously.

In this paper, we used nanosphere lithography method to fabricate nano cone array on silicon (Si) wafer as Fig. 1 shows. This nano structure can reduce optical reflection of Si surface and enhance absorption efficiently in the visible spectrum. Moreover, an ultrathin 13 nm thickness gold (Au) film was sputtered on the nano cone array, by which surface plasmon can be excited and the absorption in the near-infrared region can be greatly enhanced. We also gave a comprehensive analysis on the enhancement mechanism by theory and experiment. The nano cone array on Si wafer is fabricated by a controlled colloidal sphere lithography, which has been widely exploited in the fabrication of nano structures, possessing advantages of large area, low cost, and easy fabrication process.

2. Experiment design and fabrication

We use a self-assembled nanosphere lithography to fabricate the nano cone array on the Si substrate, which is an efficient and inexpensive method to fabricate a large-area nanostructure. The procedure for the fabrication is shown in Fig. 1. Before making the PS sphere mask, silicon wafers (500 μm thickness, n-type (100)) were ultrasonically cleaned subsequently in acetone, ethanol, and distilled water for 30 min. The commercial PS spheres (700 nm) in an aqueous solution (10 wt %) were mixed up with equal volume of ethanol. Then the Si wafer were placed in a plastic box. The plastic box was filled up with deionized water. We use a syringe pump to inject the mixed PS sphere liquor onto the water surface at a rate of 3 μL/min. The PS spheres spread on the water surface and the surface tension forced the PS spheres to form a well-order monolayer over a large area on the water surface by the interface self-assembly method as the description in references [29,30]. The well-order monolayer would fall onto the surface of the Si wafer when the deionized water was drained out by a micropump. Then the Si wafer with the well-order PS sphere monolayer was kept in an annealing furnace at 180 °C for 5 min to make the PS spheres form good contact on the Si substrate. The size of the PS spheres was reduced by oxygen plasma using reactive ion etching (RIE) in a controlled manner. Afterward, we continued to etch silicon by RIE using SF_6 and O_2 plasma with 24 mTorr pressure, 50 w RF power, 48 sccm SF_6 flow rate, and 12 sccm O_2 flow rate. The formation mechanism of the nano cones can be understood by the chemical reactions during the RIE process. The active fluorine ions from the SF_6/O_2 plasma provide an etching effect to Si by forming the volatile SiF_4. As the etching rate of polystyrene sphere is much lower than that of Si under SF_6/O_2 plasma etching, polystyrene nanospheres protect Si immediately underneath them from being etched, resulting in the formation of nano cone array directly on Si wafer [31]. After RIE procedure, well-aligned nano cones can be formed on the entire silicon wafer. We removed the remaining PS nanospheres using ultrasonic cleaning in toluene solution for 10 min. Finally, an ultrathin 13 nm thickness Au film was coated on the silicon nano cones substrate by sputtering deposition in a vacuum chamber. In this fabrication process, the period can be adjusted by the different sizes of the PS spheres, the basal diameter and the height of the nano cone can be controlled by different etching time of the RIE procedure; the thickness of Au layer is determined by the deposition process. The experimental reflectance (R) and transmittance (T) are measured using a spectrometer (PerkinElmer Lambda-1050) equipped with a 160 mm integrating sphere. The experimental absorptance (A) is calculated by subtracting the sum of normalized reflectance and transmittance from unity.

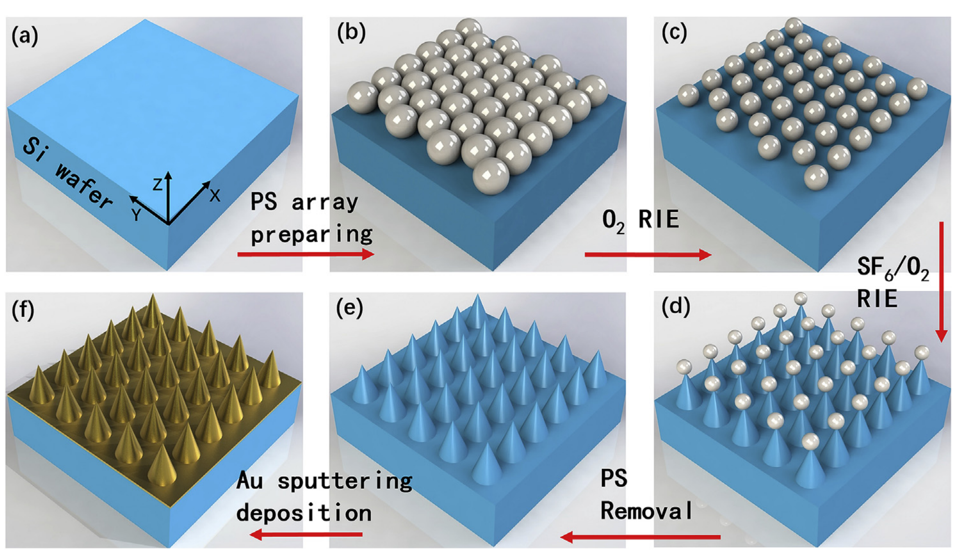

Fig. 1. Schematic illustration of the fabrication of nano cone array on silicon wafer. (a) A cleaned 500 μm thickness n-type Si (100) wafer. (b) A close packed PS monolayer template on the silicon wafer. (c) The size of the PS spheres was reduced by oxygen plasma etching. (d) Nano cone array with PS 'caps' was formed directly on Si wafer after SF_6/O_2 plasma etching. (e) The remaining PS nanospheres were removed. (f) Au film was coated on the nano cones by the method of RF reactive magnetron sputtering.