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Periodic arrays of nanopores made on single-crystalline silicon substrates with a self-assembled lithographic process

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ABSTRACT

We report here the fabrication of periodic arrays of size- shape-, and spacing-controllable Si nanopores on single-crystalline (110)Si and (111)Si substrates by using our proposed approach, which is based on the self-assembled polystyrene nanosphere lithography in conjunction with the use of oxygen plasma treatments and KOH anisotropic etching processes. Compared with other works, the facile approach proposed here offers a much simpler and low-cost scheme which does not require the use of additional metal-film hard masks deposition and stripping processes. By adjusting the KOH etching duration, the Si nanopore size can be effectively tuned and controlled. The Si nanopores formed on (110)Si and (111)Si were found to be heavily faceted, and their faceted morphologies were mainly determined by the crystal orientations of the Si substrates used. Furthermore, the results of the ultraviolet-visible spectroscopic measurements revealed that the (110)Si substrate with nanopore arrays exhibited significant antireflection properties, and its optical reflectance was found to decrease with increasing the etched nanopore size. The obtained results present the exciting prospects that the combined approach presented here could have significant potential for use in Si-based optoelectronic devices.

1. Introduction

Recently, studies of structures and optical properties of surface-textured semiconductors have drawn much attention, because well-ordered textured surface structures possess potential applications in advanced optoelectronics, nanophotonics, and microelectromechanical systems [1–3]. Among these surface-textured semiconductors, silicon-based (Si-based) substrates with nanopore-textured surfaces are particularly attractive due to its excellent light-trapping properties and technical compatibility with existing Si-based semiconductor processing technologies [4–6]. Therefore, many recent research efforts have been devoted to develop template-patterning approaches to produce highly-ordered nanopore structures on Si substrates at high throughput and low cost. One of promising nanopatterning techniques is the self-assembled nanosphere lithography [7–11]. In this technique, a monolayer of colloidal nanospheres formed on blank-Si substrate by self-assembly was utilized as the metal-film deposition template. After metal-film hard mask deposition and subsequent Si etching and hard mask stripping processes, periodic Si nanopore arrays were produced on the surfaces of Si substrates. Although these self-assembled nanosphere lithographic methods provide more efficient fabrication processes compared to the conventional lithographic methods, the self-assembled lithographic approach is still limited by the necessity of using additional metal-film hard mask deposition and stripping processes. To overcome the aforesaid limitations, we recently developed an alternative high-throughput, cost-effective nanopatterning approach, which combines the oxygen-plasma modified nanosphere lithography and KOH anisotropic etching processes. Our recent study has demonstrated that our proposed nanosphere-templated etching method is an effective nanopatterning approach for the fabrication of well-ordered arrays of Si nanopores on Si substrates [12]. However, it is worthwhile to note that most of the Si nanopores formation studies were carried out on (001) oriented silicon substrates. The studies on controlling the formation of well-ordered Si nanopore arrays on differently oriented silicon substrates via the nanosphere-templated etching technique are extremely rare. In addition, previous studies have also reported that the optical reflection properties of Si substrates were significantly affected by the produced textured surface microstructures [13,14]. Therefore, it is of both fundamental and scientific interests to investigate further the morphological and structural evolutions of Si nanopores produced on various single-crystalline Si substrates.

In the present study, we show the fabrication of two-dimensional (2D) well-defined, periodic arrays of Si nanopores on single-crystalline (110)Si and (111)Si substrates by employing our proposed approach. The surface morphologies, dimensional evolutions, and optical reflection behaviors of Si nanopores produced under different etching conditions are also studied.

2. Experimental procedures

Single-crystal, boron-doped (110)Si and (111)Si wafers were used as the substrates in the present study. Both wafers were cut into pieces

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with size of 0.8 cm × 0.8 cm. Monodispersed polystyrene (PS) spheres with a mean diameter of 500 nm were utilized to form a self-assembled PS sphere monolayer on the single-crystalline Si surfaces according to the procedures described elsewhere [15,16], which served as the nanosphere lithography templates. Prior to the PS sphere monolayer deposition process, all of these (110) and (111)Si substrates were cleaned chemically using a standard procedure, followed by dipping in a dilute hydrofluoric acid (HF) solution ($HF:H_2O = 3:100$) to remove the native oxide layer. After the self-assembled, a close-packed PS sphere monolayer was deposited on cleaned Si substrate, the diameter of the PS spheres was trimmed to desirable levels by using the oxygen plasma treatments. The oxygen gas flow rate and the plasma power used were kept at 1 sccm and 50 W, respectively. Subsequently, the obtained samples were immediately immersed in a 25 wt.% KOH etching solution. No additional metal thin films are needed to be deposited on the Si substrates as hard masks for etching. The KOH anisotropic etching was performed at 20 °C for various etching time. Following the KOH etching process, the oxygen plasma-trimmed PS sphere templates were lifted off in tetrahydrofuran solvent under ultrasonic agitation.

The surface morphology, size, shape, and periodicity of the obtained PS sphere array templates and the KOH etched Si nanopore arrays were systematically examined by scanning electron microscopy (SEM, Hitachi S-3000H, operated at 10 keV). An ultraviolet–visible (UV–Vis) spectrophotometer (PerkinElmer Lambda-35) equipped with an integrating sphere was used to evaluate the optical reflectance of the Si substrates with various-sized periodic nanopore arrays. Prior to the UV–Vis measurements, all of the blank- and KOH-etched Si samples were dipped in a dilute HF solution to remove the surface oxide layer. Transmission electron microscopy (TEM, JEOL JEM-2000 FXII, operated at 160 keV) and high-resolution TEM (HRTEM, JEOL JEM-2100, operated at 200 keV) were utilized for microstructure characterization. The procedures for preparing the TEM specimens have been reported in detail previously [17]. X-ray photoelectron spectroscopy (XPS, Thermo VG-Scientific Sigma Probe) equipped with an argon ion beam (3 keV, 127 $\mu A/cm^2$) system was used to examine the chemical composition of the Si substrate surface after O_2 plasma treatment.

3. Results and discussion

Fig. 1 (a) shows a representative SEM image of a close-packed monolayer of 500-nm-diameter PS spheres on the surface of Si substrate by self-assembly. The diameter of the PS spheres can be effectively reduced and controlled by using an appropriate oxygen plasma treatment. An example is shown in Fig. 1 (b). In this study, the average diameter of the oxygen plasma-trimmed PS spheres was about 400 nm. The obtained hexagonal nonclose-packed PS sphere monolayer was then utilized as the template for the subsequent etching process. After the nonclose-packed PS spheres-masked Si substrate etched in aqueous KOH solution and lift-off of the PS sphere templates, 2D well-ordered arrays of Si nanopores with uniform size and spacing were produced on single-crystalline Si substrates. An example of such Si nanopore array on the surface of (110)Si substrate fabricated at 20 °C for 15 min is shown in Fig. 1 (c). It can be clearly seen from the high-magnification SEM image (the inset in Fig. 1 (c)) that the Si nanopores are hexagonally arranged and exhibit a faceted morphology with rounded corners. To further investigate the evolution of the size and shape of Si nanopores formed on (110)Si substrate with the KOH etching time, the nonclose-packed PS spheres-masked (110)Si substrates etched at the same temperature for different periods of time were systematically examined by SEM.

Fig. 2 (a)–(c) show the representative top-view SEM images of periodic Si nanopore arrays on (110)Si substrates produced in the KOH etching solution at 20 °C for 25, 35, and 45 min, respectively. As can be seen in these SEM images, all the KOH-etched Si nanopore arrays have the same hexagonal periodicity as that of the oxygen plasma-trimmed PS sphere template used in this study. The corresponding high-magnification SEM images, as shown in Fig. 2 (d)–(f), further revealed that increasing the KOH etching time would lead to a larger average size of Si nanopores. The characteristic size of the Si nanopore is defined in Fig. 2 (e). Based on the results of SEM observations, it can be inferred that the KOH etching reaction starts at the central part of the Si nanopore and then propagates laterally and downward. In addition to the increased size, the edges of the faceted Si nanopores formed on (110)Si gradually become sharper and more pronounced as the etching time increased, but the shape of the faceted Si nanopores fabricated for different etching time did not significantly change. It is also obvious from the SEM images that the Si nanopores formed on (110)Si were heavily faceted. Actually the etching pits with faceted morphology have already been formed for an etching time as short as 15 min (Fig. 1 (c)). Silicon crystal is known to have the diamond cubic structure, thus the orientation indices of the faceted edges and planes of Si nanopore can be readily identified by measuring the angles relative to the Si substrate coordinates. Fig. 3 shows a typical top-view SEM image of an individual faceted Si nanopore produced on (110)Si surface. In Fig. 3, the faceted edges of the Si nanopore in hexagon-like shape were identified to be parallel to $<\bar{1}1\bar{2}>$, $<1\bar{1}\bar{2}>$, and $<1\bar{1}0>$ Si directions, and the two exposed inclined planes are (111) and $(11\bar{1})$ crystallographic planes which have the lowest surface energy in silicon [18,19].

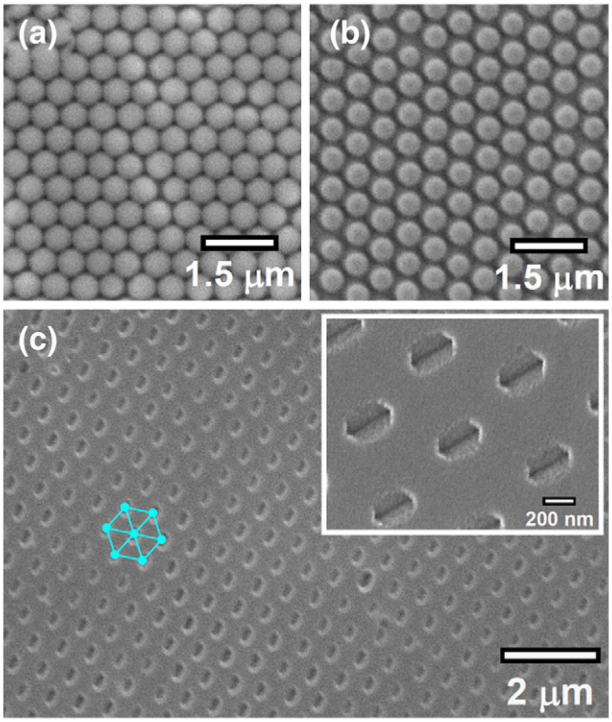

Fig. 1. Top-view SEM images of a hexagonal PS spheres monolayer on Si substrate (a) before and (b) after the O_2 plasma treatment. (c) A typical top-view SEM image of a periodic Si nanopore array fabricated on (110)Si substrate. The inset is the corresponding high-magnification SEM image.

The optical characteristics of the (110)Si surfaces with and without Si nanopore arrays were evaluated using a UV–visible spectrometer with an integrated sphere. Fig. 4 (a) shows the measured total reflectance spectra of nanopore arrays on (110)Si substrate fabricated for different KOH etching time durations. Compared to the blank-(110)Si substrate that shows a total reflectance of about 30–50% in a wavelength (λ) range of 400–800 nm, the reflectance of the nanopore-textured Si surface is greatly decreased. The measurement results shown in Fig. 4 (a) also reveal that longer KOH-etching duration would lead to a lower optical reflectance, and the lowest total surface