Fabrication and optical properties of silicon nanopillars

L S Golobokova, Yu V Nastaushev, F N Dultsev, D V Gulyaev, A B Talochkin and A V Latyshev
A.V. Rzhanov Institute of Semiconductor Physics of SB RAS, 13 pr. Lavrentieva, Novosibirsk 630090, Russia
E-mail: GolobokovaLS@isp.nsc.ru

Abstract. The optical properties of ordered arrays of silicon nanopillars (Si NPs) were investigated. Electron Beam Lithography (EBL) followed by Inductively Coupled Plasma Reactive Ion Etching (ICP-RIE) was used for Si NPs fabrication. Si NPs were chemically and electrically passivated through the deposition of TiONx nanolayer. The silicon nanopillars were characterized by using scanned electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM). We demonstrate that a various colors can be obtained by exploiting the resonant light scattering properties of individual Si NP. In addition the low temperature photoluminescence from Si NPs was investigated. The peak photoluminescence energy was observed at 0.83 µm and 1.14 µm. Raman scattering enhancement was found too.

1. Introduction
Silicon nanopillars are of interest due to their potential application in various fields: microelectronics [1], optoelectronics [2], photonics [3, 4], photovoltaics [5, 6], biology [7], and sensors [8, 9]. Various groups have reported strong antireflective properties in Si NPs [10, 11], and in other nanoscale structures [12]. The authors [13] have demonstrated enhanced photoluminescence (PL) and second harmonic generation (SHG) in SiNPs. SiNPs can be formed by means of different methods including vapor-liquid-solid growth, silver induced chemical etching and e-beam [14] or laser interference lithography [15] followed by dry etching. In the present paper, we studied the morphology and optical properties of Si NPs, fabricated using electron-beam lithography (EBL) followed by dry etching. The most controlled way of top-down process is using lithography to define a mask pattern followed by RIE. EBL is a well-established high resolution patterning technique. The plasma etching is capable of providing an anisotropic profile. Therefore, the diameter and the length of the Si NPs can be precisely controlled using EBL and plasma etching.

2. Experimental
The «top-down» approach was used to fabricate silicon nanopillars by means of e-beam lithography and deep reactive ion etching (RIE). Prime silicon wafer (n-type) <100> was used as a base material. The substrates were cleaned in isopropyl alcohol for 3 minute using an ultrasonic cleaner and rinsed in de-ionized water. Then, silicon substrates were cleaned with fresh solution (H₂O₂ : NH₄OH : H₂O = 1 : 1/5 : 5). They were baked at 200°C and cooled to room temperature immediately before coating. Then, e-beam resist ma-N2403 was spincoated and heated on a hotplate at 90°C for 1 minute. Various viscosities of the ma-N2403 resist were used resulting in film thicknesses of 180 and 300 nm. The resist coated wafers were exposed to pattern a dense nanopillars array. Raith 150 (Raith GmbH) was used as a lithography system for nanometer patterning. The electron dose was varied within the range...
of 0.01÷0.1 pC per dot. After exposure, development process was carried out using ma-D532 developer. Then the samples were rinsed in deionized water and blown to dry. Figure 1 shows a SEM image of pattern in resist as the mask of NPs before etching. The diameter of the NP pattern in the resist as a function of dose is shown in figure 2. As shown in figure 2, the resulting diameters of NP in the resist are linearly dependent on the applied point dose. The patterns for nanopillars were designed using RAITH ELPHY Quantum GDSII Editor. Silicon was etched into nanopillars using the resist as a mask in an ICP-RIE plasma etcher (Oxford Plasmalab 100). Two different fluorinated etch chemistries were utilized: a SF₆/O₂ cryogenic etch and the Pseudo-Bosch (SF₆/C₄F₈). It should be noted that the SF₆/O₂ cryogenic etching process limited the height of the Si NPs. In order to enhance the height of pillars, we utilized the Pseudo-Bosch process. The Bosch process used a two-step plasma process which alternates between etching in SF₆ flow and passivation in C₄F₈ flow. Sidewall protection is achieved by C₄F₈ gas. Polymer deposition for protecting lateral sidewalls makes for a good sidewall profile for the nanopillars. Si NPs with diameters ranging from 60 nm to 350 nm with heights from 100 to 600 nm were fabricated (pitch from 0.4 µm to 1.7 µm).

![Figure 1. SEM image of the NP pattern in the resist, pitch 800 nm (tilt angle = 54°, the scale bar is 200 nm).](image1)

![Figure 2. The diameter of NP in the resist as a function of dose value.](image2)

![Figure 3. (a) A low-magnification TEM image of a Si NP. (b) HRTEM image taken near the edge of the individual NP.](image3)
As shown in figure 4 (b, c) well aligned and patterned SiNPs were observed. Si NPs were covered with a dielectric nanolayer of TiONx, formed by plasmachemical nitridation of Ti nanolayer, in order to achieve chemical and electrical passivation and stabilization of Si NP surface. The morphologies of the samples were characterized by scanning electron microscopy (CROSS BEAM 1540XB) and high-resolution transmission electron microscopy (JEM-4000EX).

In order to analyze the structure of Si NP, HR TEM characterization was performed. The Au layer was evaporated on to the samples. The thickness of the Au layer was 300 nm. As shown in figure 3, the Si NPs are single crystalline. In figure 3 transmission electron micrograph shows that the etch sidewalls are smooth.

3. Results and discussion

In recent years, vivid colors have been demonstrated by means of SiNPs [1, 16, 17]. In this work, the sample inspection has been done with Zeiss AxioImager Z1 high-performance research microscope with darkfield (DF) and brightfield (BF) optical detection. Figure 4(a) shows a bright-field image of the vertical SiNPs arrays (50×, NA = 0.8). Figure 4 (b, c) shows SEM images of these Si NPs arrays. The pitch in all of arrays is 630nm. Figure 5(c, d) shows bright-field images of the vertical SiNPs arrays (50×, NA = 0.8). Figure 5 (a, b) shows SEM images of these Si NPs arrays (pitch 400 nm). NPs with different diameter appear distinctly different colors. The image is taken with the incident light normal to the sample. It should be stressed that generated colors are dependent on the NP diameter. The colors were created by individual SiNPs. This effect had originated not from diffractive effects of the arrays. The Si NP is a dielectric nanocavity. We guess that the SiNPs exhibit Mie resonances in the visible spectral region. Bezares F J et al [2013] investigated the behavior of the Mie resonances in cylindrical Si NPs as a function of pillar diameter (68 – 260 nm) and pitch (200 – 500 nm).

![Figure 4. A bright-field image (a) and SEM images (b, c) of Si NPs array with 630 nm pitch (tilt angle = 54°, the scale bars is 1 μm).](image)
Figure 5. SEM images (a, b) and bright-field images (c, d) of Si NPs array with 400 nm pitch (tilt angle = 54°, the scale bars is 1µm). Diameters: 280 nm (a) and 330 nm (b).

Figure 7 shows a SEM image of NPs array. In contrast to above results, figure 6 shows a dark-field image of these Si NPs, the light source incident angularly to the SiNP array. The image demonstrates the color generation due to the diffractive effects. The color observed for a given array can also be tuned by changing the angle of the incident light and changing the space orientation. Tunable structural color generation from vertical silicon NPs arranged in different square lattices is realized using diffraction.

Figure 6. A dark-field optical image of Si NPs with 1 µm pitch. The scale bar is 200 µm.

Figure 7. SEM image of Si NPs array №1 with 1 µm pitch (tilt angle = 54°). The scale bar is 100 nm.

Low temperature photoluminescence (PL) of Si NPs was investigated. Figure 8 presents the PL spectra of Si NPs. The PL spectra were measured at 4.9 K. The excitation beam from a He-Ne laser (λ = 632.8 nm) was focused onto the sample placed in a cryostat. The diameter of the focused spot was 200 µm. The peak photoluminescence energy was observed at 0.83 µm and 1.14 µm. Enhanced Raman scattering from coupled vertical Si NP arrays was observed. Enhancement at least by a factor of 40 in comparison with bulk silicon was achieved.
4. Conclusion
In this work, ordered SiNPs arrays with controllable sizes were fabricated by means of e-beam nanolithography and dry etching. The ordered arrays of Si NPs fabricated by means etching present the advantages of being very uniform and defect free. This process allows fabricating dense NPs arrays with a wide range of dimensions. Ordered SiNPs arrays with diameters increasing from 60 to 350 nm were fabricated in square arrays. Si NPs were chemically and electrically passivated throughout the deposition of TiONx nanolayer. Using scanning electron microscopy, surface imaging and elemental analyses of structures were carried out. Vivid colors were demonstrated in Si NP. The enhancement of Raman scattering was investigated. The low temperature photoluminescence from Si NPs was investigated. The peak photoluminescence energy was observed at 0.83 µm and 1.14 µm. The enhanced optical properties can be achieved by optimizing the diameter and the pitch of Si NP. The results of the work show that Si NPs could be advantageous for nanoscale optical application.

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