Study of nonlinear optical phenomena in silicon nanowires

V A Mastalieva¹, V Neplokh¹, V A Morozov¹, A A Nikolaeva², A S Gudovskikh¹, I S Mukhin¹,² and S V Makarov²

¹ Department of Physics and Astronomy, Renewable Energy Laboratory, Saint Petersburg National Research Academic University, 8/3 Khlopina, SP 194021, Russia
² Faculty of Photonics ITMO University, 49 Kronverk Sky pr., SP 197101, Russia
³ Graduate School of Physics and Materials Technology, Peter the Great St. Petersburg Polytechnic University, 29 Politekhnicheskaya, SP 195251, Russia

strindberg76@mail.ru

Abstract. This work studies generation of second and third harmonics in arrays of vertically oriented silicon nanowires (SiNWs) encapsulated into a silicone membrane and separated from the growth substrate. The structures were produced by plasma-chemical etching of silicon substrate resulting in a formation of homogeneous arrays of SiNWs. Such SiNW-based membranes demonstrated efficient infrared-to-visible light conversion by generation of second and third harmonic signals visible by a naked eye. This study contributes to the development of technology of optical devices based on silicon and presents a new route for visualization of infrared radiation.

1. Introduction

Converters of infrared (IR) radiation to the visible range are in demand for various optoelectronic devices [1, 2], visualizers of IR radiation, and other nonlinear optical applications. Commercial IR visualizers are based on ceramics which are very sensitive and do not require activation by light [3, 4]. However, ceramic visualizers have limited optical transparency and mechanical flexibility and emit light at a fixed wavelength, making it impossible to distinguish between different wavelengths of incident IR radiation. A new alternative approach for visualization of IR radiation based on the generation of the second harmonic (SHG) in arrays of GaP nanowires (NWs) transferred into transparent silicone membrane was presented in our article [2].

The presented GaP NWs-based silicone membranes double the frequency of incident radiation allowing visualization of IR radiation in the range of 800-1400 nm [5]. However, the fabrication of such membranes requires expensive molecular beam epitaxy. In this work, we propose an approach similar to [2] based on SiNWs. Bulk silicon has an efficient third harmonic generation (THG), while only the silicon surface has SHG due to a crystal symmetry violation. Thus, SiNW arrays having large surface area and encapsulated into optically transparent silicone represent a promising object for studying nonlinear optical phenomena. Due to the developed surface of NWs, such membranes allow the study of SHG, while SiNW volume provides a significant THG signal. SiNW membranes can be used for integration with silicon electronics optical devices, including development of optical information transmission technologies [6].
2. The process of obtaining structures

2.1 Photoconverting structures based on vertically oriented structures on silicon obtained by dry plasma-chemical etching at cryogenic temperatures

The substrates with the applied mask were placed in the etching chamber and cooled to -140°C. The substrates were kept for 20 minutes to stabilize the temperature. Then, silicon was etched under the next conditions: ECP power - 30 W, ICP power - 1000 W, pressure - 5 mTorr, oxygen O$_2$ - 11 ssm$^3$min$^{-1}$, SF$_6$ flow - 50 ssm$^3$min$^{-1}$, bias voltage - -100 V

SEM image of the surface of a silicon wafer covered with a mask of latex spheres and the result of cryogenic etching is shown in Figure 1 [1].

![Figure 1](image1.png)

**Figure 1.** SEM image of the surface of a silicon wafer covered with a mask of latex spheres (a) and after cryogenic etching (b).

To reduce the diameter of the spheres, the spheres were etched in oxygen. The etching result is shown in Figure 2a.

![Figure 2](image2.png)

**Figure 2.** SEM image of the surface of a silicon wafer covered with a mask of latex spheres etched in oxygen plasma (a) and after cryogenic etching under such a mask (b).

The cross-sectional SEM image (Fig.2b) demonstrates that etching with such a mask makes it possible to obtain vertically ordered structures from silicon fibers.[1]

2.2 Nanospheric lithography 0.9 μm for silicon oxide

For the deposition of spheres, an initial 10% by mass solution of 0.9 μm spheres in water was taken. The solution requires preliminary preparation. First, the solution is placed in an ultrasonic bath to
increase the homogeneity of the solution. Next, 500 μl of the solution is withdrawn using a mechanical pipette dispenser and placed in a centrifugal tube. Then the solution is centrifuged at a speed of 13,400 revolutions for 4 minutes. As a result, the latex spheres settle to the bottom of the tube and you can take out excess water using a dispenser. Next, isopropyl alcohol is added. By varying the ratio of alcohol / water, you can control the viscosity of the solution, surface tension and potential. The dose was selected in such a way that 1000 μL of the solution was applied to the substrate. After adding alcohol, the solution is additionally kept in an ultrasonic bath at 50 °C. Then, the following parameters were used on the centrifuge to apply the resist: the sphere's deposition rate was 300 rpm; drying speed 900 rpm; low acceleration [1].
A four-inch Si substrate completely covered with a single monolayer of close-packed polystyrene spheres is shown in Figure 3. A further increase in the concentration of isopropyl leads to the formation of two or more monolayers. An image of the resulting structure can be seen in Figure 3 [1].

![Figure 3. Si substrate 100 mm in diameter completely covered with one monolayer of spheres.](image)

Using this optimal water / isopropyl solution allows us to obtain one monolayer in a tightly packed package for complete coverage of the substrate. In addition, this method makes it possible to regulate the surface concentration of the spheres by changing the concentration of isopropyl in the solution [1].

3. Study of SHG and THG signal

3.1. Samples fabrication
The SHG and THG has been studied in arrays of vertically oriented SiNWs encapsulated into a silicone membrane and peeled from the growth substrate. NWs were produced by plasma-chemical etching of bulk silicon substrates resulting in arrays of vertical-oriented nanostructures. Dense monolayers of SiO₂ spheres served as masks for microsphere lithography. The length of obtained NWs was about 6 μm, while diameter was about 1.5 μm. SEM image of structures is shown in the picture 4.

![Figure 4. SEM image of the investigated structures. Image a) cross-section whiskers obtained by etching and b) an array of whiskers on a substrate at an angle of 45 degrees.](image)
Further, the NW arrays were encapsulated into a polymer matrix and separated from the growth substrate. This technology enables not only reuse of growth substrates, but also combination of various material systems in order to create ultra-thin (up to several microns thickness) flexible transparent functional structures, and fabrication of large area (up to 50 sq. cm.) samples. The harmonic generation indicators are shown in the Figure 5.

![Figure 5](image.png)

**Figure 5.** Images of the measurement results – a) generation of the second and b) third harmonics on the sample.

### 3.2. Measurements of SHG and THG

The SHG and THG signal was measured using a setup of IR femtosecond laser and spectrometer operating in the visible spectral range. The laser power before the objective was 30 mW, and 3 mW after the objective, the fluence was $12 \times 10^{-3}$ mJ/cm$^2$. Under these excitation conditions the samples generated a THG signal visible by a naked eye in the range of 400-600 nm (1200-1800 nm of incident IR radiation, respectively). In Figure 6, you can see the graphs of the dependence of the wavelength on the intensity with the indicators of the third harmonic generation on the surface of the sample. Figure 7 shows the glow of points on the surface of the sample with different wavelengths.

![Figure 6](image.png)

**Figure 6.** Graph with the third harmonic generation index of 490 nanometers a) without ultraviolet radiation, b) with ultraviolet light glow (third harmonic range from 400-660 nanometers).
Figure 7. Images with luminescence on the cut membrane surface.

The measured spectra also registered a strong SHG response of two orders of magnitude weaker in comparison to the THG, this may be associated with less efficient processes on the NW surface and a relatively large ratio of the NW volume to its surface area.

4. Summary
In conclusion, we demonstrated efficient IR visualizers based on SiNW/silicone membranes having THG signal visible to a naked eye. The studied structures also demonstrated a strong SHG signal, which can be further enhanced by increasing the contribution of the NW surface (via NW diameter reducing) and surface treatment. This study contributes to the further development of the physics and technology of optical devices based on silicon.

Acknowledgments
VN thanks the Russian Foundation for Basic Research (RFBR project № 19-32-60040) for PDMS/NW membrane fabrication.

References
[1] Morozov I 2020 Physico-technological foundations of microstructuring processes for the creation of vertically oriented photoconversion structures based on silicon: Dis. Cand. Tech. Sciences 161
[2] Cazzanelli M and Pavesi L 2012 Second-harmonic generation in silicon waveguides strained by silicon nitride J Nat. Mater 11 148
[3] weblink:https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=296, last accessed 16/02/2021
[4] weblink: https://www.alphalas.com/products/laser-diagnostic-tools/infrared-to-visible-converters-ir-laser-beam-visualizers-ir-detectors-ir-vis-series.html?gclid=Cj0KCQiAgomBBhDXARIsAFNyUqPq76KpwEcZf99j8kRnwNFnr8VH RF3c-RLYMy_m36inbJXCKt0EaAsVpEALw_wcB, last accessed 16/02/2021
[5] Fedorov V and Mukhin I 2020 Gallium phosphide nanowires in a free-standing, flexible, and semitransparent membrane for large-scale infrared-to-visible light conversion J ACS Nano 14 10624
[6] Castellan C and Pavesi L 2019 On the origin of second harmonic generation in silicon waveguides with silicon nitride cladding J Sci. Rep. 9 1088