# OPTICS AND LASER PHYSICS

# Optical Properties of Silicon Nanowires Obtained by Metal-Assisted Chemical Etching Using Gold Nanoparticles

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Received December 1, 2022; revised December 1, 2022; accepted December 2, 2022

Owing to their unique structural and physical properties, silicon nanowires are a promising material for electronics, photovoltaics, photonics, sensors, and biomedicine. Despite the many methods available for the synthesis of silicon nanowires, metal-assisted chemical etching is currently one of the most promising for their cost-effective production. In most works, silver nanoparticles are used as a catalyst for the chemical reaction of crystalline silicon etching. However, the use of gold nanoparticles in metal-assisted chemical etching can significantly affect the morphology and optical characteristics of the prepared samples. In this work, silicon nanowires are synthesized by metal-assisted chemical etching of crystalline silicon using gold nanoparticles. According to high-resolution scanning and transmission electron microscopy, the resulting nanowires have a diameter of about 100 nm and consist of a crystalline core about 50 nm in diameter coated with a SiO<sub>2</sub> shell about 25 nm thick with silicon nanocrystals at the interface. The porosity of the silicon nanowire arrays, which has been estimated from their specular reflection spectra and has been calculated using the Bruggeman effective medium model, is 70%. At the same time, the samples exhibit an extremely low (3-7%) total reflection in the spectral region of 250–1000 nm and an increase in the intensities of interband photoluminescence and Raman scattering compared to the initial crystalline silicon substrate, caused by the light localization effect. In addition, the photoluminescence of nanowires has been detected in the range of 500–1000 nm with a maximum at 700 nm, which is explained by the radiative recombination of excitons in silicon nanocrystals with a size of 3-5 nm.

**DOI:** 10.1134/S0021364022603098

### **1. INTRODUCTION**

At present, silicon nanowire structures are studied by many scientific groups. Such interest is due to an easy and affordable way to fabricate this material, as well as to its unique electronic and optical properties [1]. Wagner and Ellis were the first to prepare silicon nanowires (SiNWs) by the vapor-liquid-crystal method in 1964 [2]. It is worth noting that this method is rather laborious. It was found that silicon nanowires fabricated by this method contain an admixture of gold in the entire volume, which can negatively affect their electronic properties [3]. The most widely used method of manufacturing SiNWs today is metalassisted chemical etching (MACE). In MACE, wet etching of crystalline silicon (c-Si) substrates in solutions containing hydrofluoric acid (HF) and hydrogen peroxide  $(H_2O_2)$  is catalyzed by metal particles at room temperature [4-6]. Metal particles can be easily removed by chemical etching after the SiNW formation is completed, which ensures that the SiNW surface is clean from metal catalyst impurities. Other advantages of the MACE method are simplicity, low cost, and the ability to reproducibly prepare SiNW arrays over a large area. It was shown that SiNWs prepared by the MACE method have remarkable optical properties such as visible photoluminescence (PL) [7], extremely low total reflection [8], and enhancement of Raman scattering, coherent anti-Stokes light scattering [9], and interband PL [10]. At the same time, by choosing different silicon substrates and varying the SiNW layer thickness, it is possible to modify the optical properties of SiNWs. For example, it was shown in [11] that, by choosing the doping level of the initial c-Si substrate, one can obtain either completely porous or nonporous SiNWs, which will affect the visible PL intensity. In [8], the effect of the SiNW layer thickness on the total reflection (the minimum of total reflection corresponds to a SiNW layer thickness of 1- $2 \,\mu$ m) and the nonlinear dependence of the enhancement of the Raman scattering and the third harmonic generation with an increase in the SiNW layer thickness were shown. Furthermore, it is possible to additionally dope SiNWs and thereby to control their electronic properties [12, 13].

For the first time, the MACE method was used to form layers of porous silicon [14–16]. Further, this method was studied in detail, and the possibility of its use for the formation of the SiNWs was shown [4–6]. The metals commonly used as a catalyst for etching reactions are silver [17], gold [15, 18], and platinum [14]. However, the vast majority of works use silver nanoparticles deposited on the c-Si surface from a solution of silver nitrate (AgNO<sub>3</sub>) and HF. As for the deposition of gold nanoparticles to further form SiNWs, the most commonly used methods are poorly reproducible gold sputtering on a c-Si substrate [15, 18] and expensive lithography methods [19–23].

We recently proposed a new method for depositing gold nanoparticles on a c-Si substrate by their reduction from AuCl<sub>3</sub> salt in the presence of HF, which were then used in MACE to prepare SiNWs [24]. This method is much simpler, cheaper, and faster than the previously proposed sputtering and lithography methods. It allows one to prepare SiNWs on large areas in record times. However, the structural and optical characteristics of the prepared samples, which are of considerable interest for their further use in photovoltaics, photonics, sensors and biomedicine, were not studied in [24].

The aim of this work is to study the structural and optical properties of SiNWs prepared by the MACE method, where gold nanoparticles are used as a catalyst for the chemical etching of c-Si.

# 2. SAMPLES AND METHODS

Silicon nanowires were fabricated by MACE of a (100) c-Si substrate with the *p*-type conductivity and a resistivity of 10–20  $\Omega$  cm. Before the MACE procedure, the c-Si substrate was washed in acetone and isopropanol for 5 min in an ultrasonic bath (Elmasonic S15H) to remove organic and inorganic contaminants and then washed in 5 M HF for 1 min to remove natural oxide. At the first MACE stage, the c-Si substrate was immersed for 15 s in a solution of 0.01 M AuCl<sub>3</sub> and 5 M HF in a volume ratio of 1 : 1; as a result, the c-Si surface was coated with gold nanoparticles. At the second stage, the gold-coated c-Si substrate was placed for 8 min in a solution of 5 M HF and 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in a volume ratio of 10:1. Then, to remove gold nanoparticles, the sample was placed for 15 min in aqua regia (a solution of nitric (HNO<sub>3</sub>) and hydrochloric (HCl) acids in a volume ratio of 3:1). Preparation took place at room temperature. Finally, the samples were rinsed several times in Millipore water and dried at room temperature.

The structural properties of the prepared SiNW samples were studied using a Carl Zeiss SUPRA 40 scanning electron microscope and a Zeiss Libra 200FE high resolution transmission electron microscope. The total reflection spectra of SiNWs in the spectral region from 250 to 1500 nm were measured on

a PerkinElmer Lambda 950 spectrometer equipped with an integrating sphere. The specular reflection spectra in the near and mid-infrared spectral ranges were measured on a Bruker IFS 66v/S infrared Fourier spectrometer, and the interband PL and Raman spectra excited by a cw Nd:YAG laser at a wavelength of 1.064  $\mu$ m were measured in the backscattering geometry on an FRA-106 attachment of the same Bruker IFS 66v/S infrared Fourier spectrometer. To study PL in the spectral range of 500–1000 nm, excitation from a helium–cadmium laser with a wavelength of 325 nm was used. The spectra were recorded on a SOLAR TII monochromator with a CCD camera operating in the visible range of the spectrum.

## 3. RESULTS AND DISCUSSION

A scanning electron microscopy image of the SiNW arrays (side view) is shown in Fig. 1. It can be seen that SiNWs look like quasi-ordered arrays with a predominant orientation along the [100] crystallographic direction. To obtain this image, the gold nanoparticles were not removed, and they are visible as bright points at the nanowire–substrate interface. The inset of Fig. 1 clearly shows that the gold nanoparticles are located at the base of the SiNWs and hence initiate MACE of the c-Si substrate. The SiNW layer thickness after 8 min etching is about 2  $\mu$ m, the nanowire diameter is 100 nm, and the distance between them is 50–100 nm.

A transmission electron microscopy image of a single SiNW is shown in Fig. 2. It can be seen that the resulting nanowire consists of a 50-nm crystalline Si core, on which a layer of silicon nanocrystals (nc-Si) 2-5 nm in size is observed, and a 25-nm-thick SiO<sub>2</sub> shell. The formation of an oxide layer on the SiNW



**Fig. 1.** Scanning electron microscopy image of silicon nanowire arrays (side view) with gold nanoparticles initiating metal-assisted chemical etching. The inset shows an enlarged silicon nanowire fragment with gold nanoparticles.

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**Fig. 2.** (Color online) Transmission electron microscopy of a silicon nanowire.

surface occurs both during their synthesis and during the treatment of the prepared arrays in a solution of hydrochloric and sulfuric acids (the procedure for removing gold nanoparticles). Silicon nanocrystals appear because of the inhomogeneous oxidation of the nanowire surface in the MACE process.

Specular reflection spectra in the near and midinfrared ranges show interference peaks associated with interference in thin films upon the reflection of two beams from the air—SiNW and SiNW—cSi interface (Fig. 3).

The effective refractive index of SiNW arrays is calculated by the expression [25]

$$\eta_{\rm eff} = \frac{1}{2L\Delta k},\tag{1}$$

where L is the thickness of the SiNW layer and  $\Delta k$  is the distance between interference peaks in Fig. 3. The effective dielectric permittivity of samples was determined by the formula

$$\varepsilon_{\rm eff} = n_{\rm eff}^2.$$
 (2)

Within the Bruggeman effective medium model [26], the porosity of the resulting SiNW arrays is calculated the formula

$$f_{\rm air} \frac{\varepsilon_{\rm eff} - \varepsilon_{\rm air}}{\varepsilon_{\rm eff} + l(\varepsilon_{\rm air} - \varepsilon_{\rm eff})} + f_{\rm Si} \frac{\varepsilon_{\rm eff} - \varepsilon_{\rm Si}}{\varepsilon_{\rm eff} + l(\varepsilon_{\rm Si} - \varepsilon_{\rm eff})} = 0, \quad (3)$$

where  $\varepsilon_{air} = 1$  is the permittivity of air,  $\varepsilon_{Si} = 11.8$  is the permittivity of silicon, l = 0.5 is the depolarization factor for a cylinder (SiNWs look like elongated objects closer in shape to a cylinder than to a sphere or plane),  $f_{air}$  is the air filling factor (porosity of SiNW arrays), and  $f_{Si}$  is the silicon filling factor; in this case,

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**Fig. 3.** (Color online) Specular reflectance spectrum of silicon nanowire arrays in the near and mid-infrared spectral ranges.

 $f_{\text{air}} + f_{\text{Si}} = 1$ . The porosity of the SiNW arrays calculated according to this model was 70%.

Figure 4 shows total reflection spectra of the original c-Si substrate and SiNW arrays. A characteristic spectrum is observed from the silicon substrate, where the total reflection is about 30% in the strong absorption region ( $\lambda < 1 \ \mu m$ ) and about 50% in the transparency region ( $\lambda > 1 \mu m$ ), since the front and back sides of the substrate are involved in the reflection. However, for SiNW arrays in the strong absorption region, an extremely low total reflection (3-7%) is observed. Thus, the resulting SiNW arrays can be used to produce an antireflection coating in photovoltaics ("black silicon"). This effect was observed earlier for samples with SiNWs fabricated by MACE with silver nanoparticles [8] and is explained by strong scattering and absorption of light, which leads to its partial localization in the SiNW arrays.

The effect of light localization in SiNWs can also be confirmed by comparing the spectra of interband PL (broad band) and Raman scattering (sharp peak at 520 cm<sup>-1</sup>) of the original c-Si substrate and SiNW arrays (Fig. 5). The position and shape of the Raman peaks for SiNWs are similar to the c-Si substrate, which indicates that the crystal structure of the sample is preserved, and the quantum confinement effect for Raman scattering is not manifested, since the diameter of the nanowires is rather large (~100 nm). The PL and Raman scattering intensities for SiNWs increase by a factor of 3 and 4, respectively, as compared to the c-Si substrate. The same results were observed for SiNWs prepared by MACE using silver nanoparticles [10] and can be explained by strong scattering and partial localization of light in an inhomogeneous optical medium.



**Fig. 4.** (Color online) Total reflection spectra of the (*1*) initial c-Si substrate and (*2*) silicon nanowire arrays.

Along with interband photoluminescence, photoluminescence was also detected in the SiNW arrays in the spectral region of 500–1000 nm with a maximum at 700 nm (photon energy of 1.77 eV); the corresponding PL spectrum is shown in Fig. 6.

Such PL of SiNW arrays in the visible and nearinfrared spectral regions can be explained by the radiative recombination of excitons in small Si nanocrystals [7]. Indeed, such Si nanocrystals are clearly visible at the silicon core—oxide shell interface in transmission electron microscopy images (Fig. 2). The average size of Si nanocrystals can be calculated from the formula [27]

$$hv = E_{g} + \frac{3.73}{d_{nc-Si}^{1.39}},$$
(4)

where *h*v is the position of the PL maximum in electronvolts,  $E_{\rm g} = 1.12$  eV is the width of the c-Si band gap, and  $d_{\rm nc-Si}$  is the size of silicon nanocrystals in nanometer. As a result, for a photon energy of 1.77 eV, the average size of Si nanocrystals is about 3.5 nm. Note that the presence of PL in the spectral region of 500–1000 nm will make it possible to use SiNWs as optical sensors and luminescent labels in biomedicine.

#### 4. CONCLUSIONS

The structural and optical properties of Si nanowires prepared by metal-assisted chemical etching using gold nanoparticles as a catalyst for chemical reactions of silicon substrate etching have been studied. It has been shown that the thickness of the Si nanowire layer is about 2  $\mu$ m after 8 min of etching, and the diameter of nanowires is about 100 nm. The nanowires consist of a ~50-nm crystalline core, on which silicon nanocrystals 2–5 nm in size are observed, and an oxide shell ~25 nm thick. The sample porosity is 70%.



Fig. 5. (Color online) Interband photoluminescence and Raman scattering spectra of the (1) initial c-Si substrate and (2) silicon nanowire arrays.

The Si nanowire arrays exhibit an extremely low total reflection (3-7%) in the spectral region of 250–1000 nm, which can be explained by the light localization effect. The intensities of the interband photoluminescence and Raman scattering for Si nanowires increase by a factor of 3 and 4, respectively, as compared to the c-Si substrate, which is also explained by strong scattering and partial localization of light in an inhomogeneous optical medium. In addition, photoluminescence was detected in the spectral region of 500–1000 nm with a maximum at a wavelength of 700 nm, which can be explained by the radiative recombination of excitons in silicon nanocrystals with an average size of about 3.5 nm on a Si nanowire surface.



**Fig. 6.** (Color online) Visible photoluminescence spectrum of silicon nanowire arrays.

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These results are promising for the development of antireflection coatings based on Si nanowire arrays for use in photovoltaics, as well as for the production of optical sensors and luminescent labels.

#### ACKNOWLEDGMENTS

This study was carried out within the Development Program of the Interdisciplinary Scientific and Educational School "Photonic and Quantum Technologies. Digital Medicine," Moscow State University. We are grateful to A.A. Eliseev for transmission electron microscopy measurements. The study was carried out using the equipment of the Collective Use Center Technologies for Obtaining New Nanostructured Materials and Their Comprehensive Study, acquired by the Moscow State University under the program for updating the instrumentation base within the national project "Science and Universities" and within the Development Program of the Moscow State University. The equipment of the Educational and Methodological Center for Lithography and Microscopy, Moscow State University, was also used.

#### FUNDING

The work was supported by the Russian Science Foundation (project no. 20-12-00297).

#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

#### REFERENCES

- A. S. Kalyuzhnaya, A. I. Efimova, L. A. Golovan, K. A. Gonchar, and V. Y. Timoshenko, in *Silicon Nanomaterials Sourcebook*, Vol. 2: *Arrays, Functional Materials, and Industrial Nanosilicon* (CRC, Taylor and Francis Group, London, 2017), p. 3.
- R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. 4, 89 (1964).
- J. E. Allen, E. R. Hemesath, D. E. Perea, J. L. Lensch-Falk, Z. Y. Li, F. Yin, M. H. Gass, P. Wang, A. L. Bleloch, R. E. Palmer, and L. J. Lauhon, Nat. Nanotechnol. 3, 168 (2008).
- K. Q. Peng, Y. J. Yan, S. P. Gao, and J. Zhu, Adv. Mater. 14, 1164 (2002).
- K. Q. Peng, J. J. Hu, Y. J. Yan, Y. Wu, H. Fang, Y. Xu, S. T. Lee, and J. Zhu, Adv. Funct. Mater. 16, 387 (2006).
- K. Q. Peng, A. J. Lu, R. Q. Zhang, and S. T. Lee, Adv. Funct. Mater. 18, 3026 (2008).
- V. A. Sivakov, F. Voigt, A. Berger, G. Bauer, and S. H. Christiansen, Phys. Rev. B 82, 125446 (2010).

- A. Efimova, A. Eliseev, V. Georgobiani, M. Kholodov, A. Kolchin, D. Presnov, N. Tkachenko, S. Zabotnov, L. Golovan, and P. Kashkarov, Opt. Quantum Electron. 48, 232 (2016).
- L. A. Golovan, K. A. Gonchar, L. A. Osminkina, V. Yu. Timoshenko, G. I. Petrov, and V. V. Yakovlev, Laser Phys. Lett. 9, 145 (2012).
- K. A. Gonchar, L. A. Golovan, V. Y. Timoshenko, V. A. Sivakov, and S. Christiansen, Bull. Russ. Acad. Sci.: Phys. 74, 1712 (2010).
- V. A. Georgobiani, K. A. Gonchar, L. A. Osminkina, and V. Yu. Timoshenko, Semiconductors 49, 1025 (2015).
- S. S. Bubenov, S. G. Dorofeev, A. A. Eliseev, N. N. Kononov, A. V. Garshev, N. E. Mordvinova, and O. I. Lebedev, RSC Adv. 8, 18896 (2018).
- A. I. Efimova, E. A. Lipkova, K. A. Gonchar, D. E. Presnov, A. A. Eliseev, A. V. Pavlikov, and V. Yu. Timoshenko, J. Raman Spectrosc. 51, 2146 (2020).
- P. Gorostiza, R. Diaz, M. A. Kulandainathan, F. Sanz, and J. R. Morante, J. Electroanal. Chem. 469, 48 (1999).
- 15. X. Li and P. W. Bohn, Appl. Phys. Lett. 77, 2572 (2000).
- S. Chattopadhyay, X. Li, and P. W. Bohn, J. Appl. Phys. 91, 6134 (2002).
- V. A. Sivakov, G. Bronstrup, B. Pecz, A. Berger, G. Z. Radnoczi, M. Krause, and S. H. Christiansen, J. Phys. Chem. C 114, 3798 (2010).
- M. K. Dawood, S. Tripathy, S. B. Dolmanan, T. H. Ng, H. Tan, and J. Lam, Appl. Phys. **112**, 073509 (2012).
- I. V. Bagal, M. A. Johar, M. A. Hassan, A. Waseem, and S.-W. Ryu, J. Mater. Sci.: Mater. Electron. 29, 18167 (2018).
- 20. F. J. Wendisch, M. Rey, N. Vogel, and G. R. Bourret, Chem. Mater. **32**, 9425 (2020).
- 21. S. Wang, H. Liu, and J. Han, Coatings 9, 149 (2019).
- 22. B. Li, G. Niu, L. Sun, L. Yao, C. Wang, and Y. Zhang, Mater. Sci. Semicond. Proc. **82**, 1 (2018).
- M. Bechelany, E. Berodier, X. Maeder, S. Schmitt, J. Michler, and L. Philippe, ACS Appl. Mater. Interfaces 3, 3866 (2011).
- 24. A. D. Kartashova, K. A. Gonchar, D. A. Chermoshentsev, E. A. Alekseeva, M. B. Gongalsky, I. V. Bozhev, A. A. Eliseev, S. A. Dyakov, J. V. Samsonova, and L. A. Osminkina, ACS Biomater. Sci. Eng. 8, 4175 (2021).
- 25. B. Rossi, *Optics* (Addison-Wesley, Reading, MA, 1957).
- D. A. G. Bruggeman, Ann. Phys. (Leipzig) 416, 636 (1935).
- G. Ledoux, O. Guillois, D. Porterat, C. Reynaud, F. Huisken, B. Kohn, and V. Paillard, Phys. Rev. B 62, 15942 (2000).

Translated by L. Mosina