Research Article

Linear and nonlinear optical response of Mie-resonant Si nanoparticles and its modification induced by femtosecond irradiation post-treatment

Denis M. Zhigunov a,*, Daniil A. Shilkin b, Vladimir O. Bessonov b,c, Ilya M. Antropov b, Dmitry A. Chermoshentsev a,e,f, Sergey V. Semin d, Alexey V. Kimel d, Andrey A. Fedyanin b

a Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, Bid. 1, 121205, Moscow, Russia
b Faculty of Physics, M. V. Lomonosov Moscow State University, Leninskie Gory 1, 119991, Moscow, Russia
f Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Prospect 31 Bid. 4, Moscow, 119071, Russia
c Russian Quantum Center, Bolshoy Boulevard 30, Bid. 1, 121205, Moscow, Russia
d Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141701, Russia

ABSTRACT

Silicon nanoparticles with Mie resonances are among the most prospective building blocks for state-of-the-art all-dielectric metasurfaces. Here we focus on linear and nonlinear optical responses of silicon nanoparticles printed by laser-induced transfer from silicon-on-insulator wafer. Second-harmonic generation and broadband multiphoton-absorption-induced luminescence are studied as a function of pump wavelength. The key role of magnetic quadrupole Mie resonances in the nonlinear optical response from silicon nanoparticles is revealed. We also show the influence of Si nanoparticle shape and structure modification, realized by additional femtosecond laser irradiation, on their linear and nonlinear optical properties.

1. Introduction

A growing surge of interest in all-dielectric metamaterials stimulates further studies aimed at deeper understanding of the fundamental properties of such artificial media [1]. Si-based Mie-resonant nanostructures attract heightened attention due to the specific role of silicon in modern technology [2]. Following the very first demonstrations of the Mie-type resonant response of Si nanoparticles (Si NPs) in the visible optical range [3-5], their optical properties became a subject of systematic research with the aim of local control of optical response at the nanoscale and fabrication of integrated silicon nanoemitters.

A pronounced enhancement of nonlinear optical response of Si NPs can be achieved due to excitation of localized resonant Mie-type modes at certain pump or emission wavelengths. Thus, an intense second- and third-harmonic generation from Si NPs was shown [6-8]. Moreover, multiphoton-absorption-induced white light emission from Si nanoparticles and from hybrid Si/Au nanoparticles was also demonstrated [9, 10], which paves the way for the creation of Si-based efficient white light local emitters. It was already shown that broadband multiphoton photoluminescence (PL) is enhanced when the pump radiation wavelength is tuned around magnetic dipole (md) Mie-resonance [9,11]. This effect is related to the enhancement of the pump electric field inside the nanoparticle and, thus, to a dramatic increase of two- and three-photon absorption rate. A further increase in the efficiency of multiphoton PL is possible by using high-Q resonances in arrays of particles [12,13] or in single particles with specific geometric parameters that ensure the excitation of quasi-bound states in the continuum [14]. For single spherical Si particles, one-photon excited PL was also shown to be enhanced when the pump wavelength approaches magnetic quadrupole (mq) resonance [11]. However, it appears that the enhancement of multiphoton PL was not experimentally studied for the pump wavelengths close to the mq resonance in the scattering spectrum.

Planar silicon nanostructures are typically fabricated using lithography techniques [2]. One of the alternative methods is laser-induced transfer (also referred to as laser printing), used in this work, which allows to create and deposit particles with controllable sizes on a broader range of substrates [15,16]. Although many techniques have been developed to fabricate and process optically resonant silicon structures, the search for new methods beneficial for specific applications is still ongoing [17,18].

Once Mie-resonant structures are fabricated, their linear and nonlinear optical response can be controlled in various reversible or irreversible ways. Reversible tuning techniques may exploit reconfigurable environments such as liquid crystal [19,20] or phase-change
materials [21], nonlinear properties of the structure itself [11,22], or excitation conditions [23,24]. Irreversible tuning can be achieved by post-fabrication irradiation leading to changes in the permittivity [25] or shape of the structure [26].

A number of studies have reported the laser-induced reconfiguration of silicon structures, including local reshaping of nanostructures and modifying the crystalline state [27]. It has been shown that irradiation of a crystalline silicon wafer with femtosecond (fs) laser light can cause the formation of amorphous, ablated, and recrystallized zones, depending on the laser fluence [28]. When, in turn, a thin amorphous silicon film is irradiated, it can transform into a nanocrystalline phase [29]. Similarly, amorphous silicon particles made by laser-induced transfer have been shown to crystallize upon irradiation with a laser pulse of appropriate power [15]. Depending on the crystalline phase, the efficiency of second-harmonic generation (SHG) from silicon nanoparticles changes significantly and reaches the highest values for nanocrystalline structures [30]. Meanwhile, to the best of our knowledge, the change in the efficiency of multiphoton PL and SHG upon modification of Si NPs by femtosecond laser light has not yet been demonstrated.

In the present paper, SHG efficiency and multiphoton-absorption-induced luminescence signal are measured for individual Si NPs as a function of the optical pumping frequency, and the obtained dependences are compared with the linear scattering spectra to reveal the role of magnetic quadrupole Mie resonances in the total nonlinear response. We also demonstrate the influence of non-reversible fs laser post-treatment on linear and nonlinear optical properties of Si NPs under study: a suppression of Mie resonances accompanied by dramatic decrease in the efficiency of SHG after additional fs laser irradiation is observed, which further supports the conclusions.

### 2. Materials and methods

Silicon-on-insulator wafer with a single-crystal 50 nm silicon layer on a 200 nm silicon oxide substrate was used as a donor for the transfer of Si NPs onto a fused quartz substrate by means of fs laser printing approach [15]. A femtosecond laser system (Spectra Physics) with 800 nm central wavelength, 50 fs pulse duration and 1 kHz repetition rate was used for Si NP fabrication. The laser beam was tightly focused on a donor substrate by means of a 50 × Nikon microscope objective lens with a numerical aperture of 0.45. Optical imaging of generated NPs was performed by dark-field microscope setup. Post-treatment of as-prepared Si NPs was done using laser irradiation provided by Coherent Mira 900 fs laser system (800 nm central wavelength, 100 fs pulse duration, 80 MHz repetition rate), which was coupled to WITec alpha300 S confocal microscope combined with a motorized XY scanning stage. Microscopic imaging of the nonlinear response of single Si NPs was performed by means of the same setup. Laser beam was focused with a 20 × Zeiss microscope objective lens into a spot of 2 μm in diameter. The detection of the nonlinear response signal was performed using an avalanche photodiode with sensitivity below 700 nm, in the spectral region defined by the transmittance of Schott BG39 cutoff optical filter used (350–800 nm). Nonlinear optical spectra were measured using a CCD camera attached to a monochromator under excitation of Coherent Hameleon laser system (tunable wavelength in the range from 680 to 1080 nm, 140 fs pulse duration, 80 MHz repetition rate). To avoid Si NP modifications, the nonlinear measurements were carried out at pump fluences of 0.3–1 mJ/cm². Optical scattering spectra were collected in forward-scattering geometry using a microscope setup equipped with Ocean Optics QE Pro spectrometer with a resolution of 2 nm. Raman spectra of as-prepared and irradiated Si NPs were measured using a micro Raman setup (Horiba Jobin Yvon LabRAM HR Evolution) in backscattering geometry with the excitation laser line at 532 nm. Scattering spectra of as-prepared Si NPs were calculated by finite-difference time-domain simulations using Ansys Lumerical software taking into account the substrate and the experimental scattering collection conditions. In the model used, a silicon particle on the glass substrate was illuminated by plane-wave radiation, and the far field scattering was calculated. The scattering was then integrated over angles corresponding to the experimental collection range. More details on the numerical model are provided in Ref. [31] (see Supporting Information, Section V). In the calculations, the dispersion of the dielectric permittivity of silicon was taken from Ref. [32].

### 3. Results and discussion

#### 3.1. Structural properties

Fig. 1 shows a dark-field microscopic image of Si NP array printed by 800 nm single fs laser pulses with the energy of about 6 nJ. The size of NPs is estimated to be about 300 nm and the shape is close to a sphere, according to scanning electron microscopy (SEM) measurements. Indeed, SEM images, taken under either normal incidence (plan view) or at 45°, show a close-to-spherical Si NP with almost no difference for both angles of view (see insets of Fig. 1). At the same time, one should consider that Si nanoparticles under study were transferred onto a glass substrate. To overcome the problem of poor charge drain due to a dielectric substrate, we used specific low-vacuum SEM operation mode, which allows obtaining much more clear images, as compared to a standard SEM operation mode, which allows obtaining much more clear images, as compared to a standard SEM operation mode, especially for supermicron size particles. This allows us to measure lateral size of Si NPs with high enough precision, however, x dimension can only be estimated based on 45° tilt images. Hence, more precise size determination was done by means of scattering spectra calculations and subsequent fitting of corresponding experimental data (see next section below), since resonance positions (especially magnetic ones) are highly sensitive to the particle size contraction in one direction [33].

Several as-fabricated NPs were subjected to irradiation post-treatment by the fs laser with pump fluences 12.5–25 mJ/cm². Throughout this manuscript, we will refer to as-prepared particles as A1—A3, and to the irradiated particles as B1–B3. The post-treatment led to significant modification of Si NP shape caused by partial local melting. This melting led to the material ejection and formation of small droplets in the vicinity of NP (see Fig. 2). In general, all irradiated NPs retained their structural integrity, hence no complete meltdown of NPs occurred under treatment conditions used.

The structure of Si NPs both before and after irradiation is crystalline, as evident from the Raman peak position near 520.5 cm⁻¹, which is a signature of the TO phonon mode of crystalline Si (c-Si), while no contribution from amorphous Si phase at 480 cm⁻¹ can be seen in Raman spectra (see Fig. 3). Asymmetry of the shape of the Raman peak for as-prepared Si NPs can be attributed to a contribution from Si

![Fig. 1. Dark-field microscopic image of Si NP array with 5 μm period printed by 800 nm single fs laser pulses with the energy of about 6 nJ. Inset: typical SEM images of a chosen Si NP, taken under 0° and 45° to the surface.](image_url)
crystalline grain boundaries, which are characterized by the intermediate Raman peak at 490–510 cm\(^{-1}\) [34–36]. This is consistent with the recent findings that laser printed Si nanoparticles may have a multigrain structure with a typical grain size of about 10 nm [7]. At the same time, no significant shift of 520.5 cm\(^{-1}\) peak (above the measurement error 0.5 cm\(^{-1}\)) is observed for both as-prepared and irradiated Si NPs. This means that, according to our data, the grain size is at least larger than 10 nm, since the latter is about an upper limit of Si crystallite size detectable through the size-dependent peak shift of Raman spectrum [37]. For some of irradiated Si NPs under study, the shape of the Raman peak becomes more narrow and, thus, almost similar to that for c-Si. It may point at the recrystallization process that likely occurs during fs laser post-treatment. At the same time, B2 NP is characterized by Raman spectrum, which is almost similar to that of as-prepared Si NP; both spectra show relatively high intensity, grain boundaries-related feature and associated asymmetric line shape. It indicates that not only pump fluence value affects the resulted degree of nanoparticle modification, but some other parameters (for instance, the exact position of the waist of the laser beam with respect to the nanoparticle site during post-treatment irradiation) also play role.

3.2. Linear optical response

Additional information about the shape of NPs can be obtained using linear scattering spectroscopy. Fig. 4 shows measured scattering spectra of as-prepared and irradiated Si NPs, as well as the corresponding numerical calculations. The observed sharp peaks correspond to electric and magnetic multipolar Mie resonances excited in single Si NP (see Fig. 4a). For a particular intact Si NP, the best agreement between experimental and calculated scattering spectra is observed for the model of spheroid with major axes equal to 326 nm (x), 326 nm (y) and 264 nm (z), where z direction is a perpendicular to the substrate surface. Such trend is characteristic for all experimental scattering spectra, while the best fit gives only small deviations of spheroid geometry within ±5 %. This behaviour can be explained by the deformation of Si NPs in z-direction, which results from their collision with the substrate surface during the transfer process [39]. Remarkably, calculated scattering spectrum for Si NP with an ideal spherical shape have no such highly pronounced experimentally observed magnetic quadrupole (mq) and octupole (mo) resonances (see Fig. 4a), which can be considered hence as signatures of nanoparticle flattening. Indeed, numerical calculations show that spectral position and intensity of magnetic resonances are highly sensitive to the particle size deformation in the illumination direction [33]. In particular, blue shift of md and mq resonances as well as rise of their intensity should be observed upon contraction of Si NP along the z axis.

Scattering spectra of irradiated Si NPs under study show almost featureless shape, hence, intense enough fs laser post-treatment leads to an almost complete smoothing of characteristic Mie-type resonances (see Fig. 4b). This fact can be attributed to a significant transformation of Si NP shape from nearly spherical to highly irregular one, accompanied by partial removal of a substance from the nanoparticle, as observed by SEM. Due to irregular character of NP shape modification, which is moreover varies from one nanoparticle to another, composition of detailed models for each particularly modified NP seems irrational. Instead, we suggest to consider simplified models of Si spheroids with different degree of deformation (for more details, see Supporting Information). Corresponding calculated scattering cross-sections show clear trend towards smoothing of scattering spectra (due to broadening or vanishing of Mie resonances) upon progress of NP shape deformation, which agrees well with our experimental findings shown in Fig. 4b.

3.3. Nonlinear optical response

The inset of Fig. 5 shows a nonlinear optical response spectra of as-prepared (A1) and irradiated Si NP (B1) taken under excitation wavelength of 780 nm, which is close to mq resonance of intact Si NP. Both the second-harmonic peak at 390 nm and a broadband multiphoton-absorption-induced photoluminescence (PL) can be seen for as-prepared Si NP. For irradiated Si NP, only SH peak is detected, while...
The observed broadband multiphoton-absorption-induced luminescence for as-prepared Si NP under study is similar to the recently reported white light emission from Si nanoparticles fabricated by laser ablation in water [9]. Less efficient yet detectable visible PL was also observed recently for bulk silicon (commercially available Si single crystal wafers) under illumination by IR femtosecond laser pulses: SH peak at 390 nm as well as broadband white light emission (PL) for each pump wavelength, the SHG intensity was determined by integrating the SH peak in nonlinear response spectrum, from which the luminescence spectrum (if any) was preliminarily subtracted. As opposed to previously reported demonstration of SHG from laser-printed Si NPs [7], here we measure its efficiency as a function of excitation wavelength, rather than NP size. Distinct correlation of SHG peak with magnetic quadrupole scattering resonance can be seen (see Fig. 6a–c), which clearly indicates the key role of Mie-type modes in SHG signal generation, in agreement with the previously reported results [7]. Unlike broadband PL, SHG peak is detected for both irradiated (B1) and as-prepared Si NPs under the same pumping conditions, although SHG intensity is more than an order of magnitude higher for the latter (see Fig. 6d and inset of Fig. 5). Both the surface and the crystalline grain boundaries, where the inverse symmetry is broken, might act as SHG sources in Si NPs. Taking into account structure modification of B1 Si NP revealed by Raman spectroscopy (absence of grain boundaries-related feature), as well as scattering resonance peaks suppression, such a pronounced SHG signal reduction can be well explained in this case (see Fig. 6d).

Microscopic images of the nonlinear optical response from single intact and irradiated Si NPs are shown in Fig. 7. Note, that both second-harmonic signal and broadband white light emission were simultaneously detected in the experiment, hence the observed bright spots reflect the positions of single Si NPs and their total nonlinear response intensity (within the detector spectral sensitivity and filter transmittance). As can be seen from comparison of Fig. 7a and b, post-treatment reduces remarkably the intensity of nanoparticle total nonlinear response (B2), or quenches it to the values, which are below the detection threshold (B3). The residual nonlinear response for B2 Si NP, which is still detectable after irradiation post-treatment, correlates with the relatively high peak intensity and the presence of contribution from Si crystalline grain boundaries in corresponding Raman spectrum (see Fig. 3). This further demonstrates that SHG intensity and white light emission from individual Si NP can be controlled by post-treatment.

**Fig. 4.** Measured scattering spectra of (a) as-prepared and (b) irradiated Si NPs. For a comparison, calculated scattering cross-sections, \( \sigma \), are plotted for a 326 × 326 × 264 nm\(^3\) spheroid and 320 × 320 × 320 nm\(^3\) sphere. Magnetic and electric dipole (md, ed), quadrupole (mq, eq) and octupole (mo) resonances are indicated. SEM images of both intact and irradiated Si NPs are shown for clarity and on the same scale (scale bar: 200 nm).

**Fig. 5.** Comparison of multiphoton-absorption-induced integral luminescence signal as a function of the pumping light wavelength, and scattering spectrum of as-prepared Si NP (A1). Inset: Comparison of nonlinear response spectrum of as-prepared (A1) and irradiated (B1) Si NPs taken under excitation by 780 nm fs laser pulses: SH peak at 390 nm as well as broadband white light emission (PL) are indicated.
however, more experiments are needed to adjust experimental conditions in order to achieve a predefined result.

4. Conclusions

To summarize, linear and Raman scattering spectroscopy, as well as nonlinear optical measurements are performed for both as-prepared laser printed Si NPs and those subjected to fs laser irradiation post-treatment. The enhancement of both second-harmonic generation and broadband multiphoton-absorption-induced luminescence is observed, when the pump radiation is in the spectral vicinity of the magnetic quadrupole Mie-resonance of intact Si NPs. This reveals the key role of magnetic modes in amplifying the nonlinear signal from Mie-resonant Si NPs, in agreement with the previously shown similar results for magnetic dipole Mie resonances. Post-treatment of as-prepared nanoparticles leads to a vanishing of Mie-type resonances in scattering spectra accompanied by a significant suppression of SHG intensity and white light emission, which is an additional evidence of the revealed enhancement factor of Mie resonances in nonlinear optical response from individual Si NPs. An ability of SHG efficiency control via fs laser post-treatment might be used for the design of metasurfaces with specified nonlinear response.

CRediT authorship contribution statement

Denis M. Zhigunov: Writing – original draft, Investigation, Funding acquisition, Data curation, Conceptualization. Daniil A. Shilkin: Writing – review & editing, Validation, Methodology, Investigation, Data curation. Vladimir O. Bessonov: Writing – review & editing, Investigation, Funding acquisition. Ilya M. Antropov: Investigation, Data curation. Dmitry A. Chermoshentsev: Software, Visualization. Andrey A. Fedyanin: Writing – review & editing, Validation, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References