Conference materials
UDC 548.75
DOI: https://doi.org/10.18721/JPM.173.241

Nonlinear optical phenomena in mesoporous SiO_2 and Si/SiO_2 nanoparticles

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Abstract. In this work we study the optical response of mesoporous SiO_2 and Si/SiO_2 nanoparticles considering different fabrication and post-synthesis treatment processes. We show that thermal annealing of mesoporous Si/SiO_2 nanoparticles transforms the Si phase from amorphous to crystalline and enhances the second harmonic generation response.

Keywords: second harmonic generation, silicon, nanostructures, mesoporous nanoparticles, IR visualizer

Funding: This work study was funded by the Russian Science Foundation no. 23-79-00018.

Citation: Mastalieva V.A., Neplokh V.V., Aybush A.V., Stovpiaga E.Yu., Eurov D.A., Vinnichenko M.Ya., Karaulov D.A., Kirilenko D.A., Golubev V.G., Smirnov A.N., Makarov S.V., Kurdyukov D.A., Mukhin I.S., Nonlinear optical phenomena in mesoporous SiO_2 and Si/SiO_2 nanoparticles, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (3.2) (2024) 207–211. DOI: https://doi.org/10.18721/JPM.173.241

Материалы конференции
УДК 548.75
DOI: https://doi.org/10.18721/JPM.173.241

Нелинейные оптические эффекты в мезопористых SiO_2 и Si/SiO_2 наночастицах

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Аннотация. В этой работе изучен нелинейный оптический отклик мезопористых наночастиц SiO_2 и Si/SiO_2 с учетом различных процессов изготовления и пост обработки. Показано, что термический отжиг мезопористых наночастиц Si/SiO_2 преобразует кристаллическую фазу Si из аморфной в нанокристаллическую и усиливает отклик генерации второй гармоники.

Ключевые слова: генерация второй гармоники, кремний, наноструктуры, преобразователи ИК излучения, мезопористые наночастицы

Финансирование: Работа выполнена в рамках проекта РНФ № 23-79-00018.

Ссылка при цитировании: Масталиева В.А., Неплох В.В., Айбуш А.В., Стовпяга Е.Ю., Еуров Д.А., Винниченко М.Я., Караулов Д.А., Кириленко Д.А., Голубев В.Г., Смирнов А.Н., Макаров С.В., Курдюков Д.А., Мухин И.С. Нелинейные оптические эффекты в мезопористых SiO_2 и Si/SiO_2 наночастицах // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 17. № 3.2. С. 207–211. DOI: https://doi.org/10.18721/JPM.173.241

Introduction

Since bulk silicon has a centrosymmetric structure, special conditions are required to demonstrate the efficient second harmonic generation (SHG) in this material. This paper proposes the use of mesoporous nanoparticles with SiO_2 framework filled with Si phase, which finds applications in the nanophotonic field [1–3].

To compare the performance of SHG at pumping in 800-1020 nm range of femtosecond laser pulses, various fabrication and processing procedures [4] were used to synthesize Si/SiO_2 and SiO_2 mesoporous nanoparticles. Infrared femtosecond laser scanning system was used for mapping [5]. It was found that thermal or laser-induced annealing of Si leads to the transformation of the Si phase from amorphous to nanocrystalline, which improves the nonlinear characteristics of the nanoparticles and makes them exhibit broadband photoluminescence. These results confirm the efficiency of mesoporous Si/SiO_2 nanoparticles for second harmonic generation and extend their potential applications in nanoscale optics [6].

Materials and methods

The synthesis process of spherical mesoporous Si/SiO_2 nanoparticles (meso Si/SiO_2 NPs) includes two steps [7]. Low-porousity monodisperse spherical SiO_2 nanoparticles (reference SiO_2 NPs) were produced through the hydrolysis of tetraethoxysilane (TEOS) in an alcohol-based solution that contained ammonia and water [4]. The synthesis process had a duration of 4 hours and resulted in a formation of 550 ± 20 nm monodisperse low-porosity (less than 15%) nanoparticles [7], which then were centrifuged and annealed at 900 °C for 5 h in air.

Monodisperse spherical mesoporous silica nanoparticles (meso SiO_2 NPs) were synthesized also by hydrolysis of TEOS [8]. The silica particles obtained were centrifuged, dried in air at 70 °C for 24 h, and annealed at 550 °C for 5 h to form the pores. The sectional pore diameter of the synthesized particles was about 3 nm, and the specific surface area and pore volume of the synthesized particles were 810 m^2/g and 0.55 cm^3/g, respectively [8].

Nonlinear Optical Response Measurements

For nonlinear optical measurements, samples from the nanoparticle colloid were deposited on pre-cleaned quenched quartz glasses. The studies were carried out using a confocal laser-scanning microscope (LSM) setup (LSM-980, Zeiss, Germany). Femtosecond laser pulses (Discovery-NX, Coherent, USA) with a repetition rate of 80 MHz, duration of 150 fs, and pulse wavelength range of 800–1020 nm were delivered through the external acousto-optic modulator (AOM) port of the LSM. The spectral characteristics of the nonlinear response were obtained at the optimum pump wavelength in the range of 900–980 nm.

Results and Discussion

An enlargement of Si clusters after annealing compared to unannealed Si/SiO_2 NPs, related to improved crystallinity due to annealing, was observed by TEM imaging (Fig. 1, *a*, *c*). The obtained TEM images allow to distinguish the nc-Si phase, which is manifested by a bright contrast being more pronounced after annealing.

The Raman measurements confirmed the amorphous state of the Si material for the as-synthesized NPs (Fig. 1, *b*) and demonstrated the presence of crystalline Si phase after annealing of Si/SiO_2 NPs, that is manifested by the peak at 518.5 cm^{-1} corresponding to the transverse optical phonon mode of crystalline Si (Fig. 1, *d*).

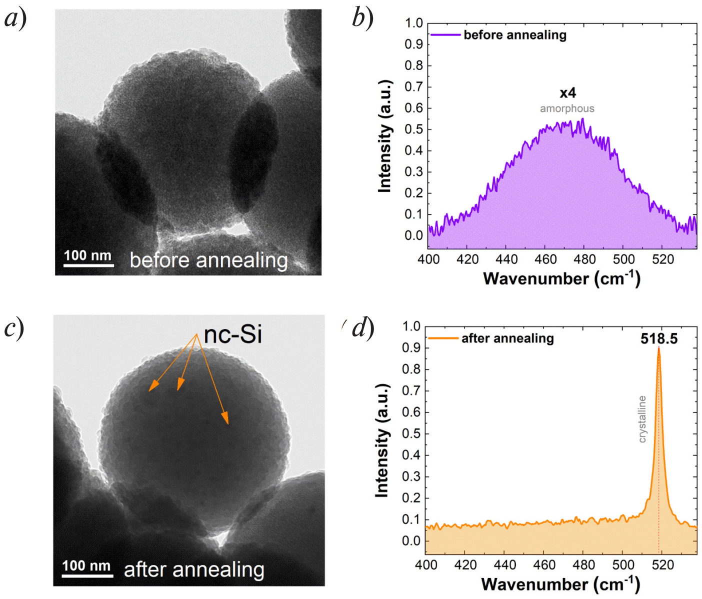

Fig. 1. TEM images of meso Si/SiO_2 NPs before (*a*) and after (*c*) thermal annealing at 850 °C. Raman spectra of meso Si/SiO_2 NPs before and after (*b*) thermal annealing at 850 °C (*d*)
For convenience, the spectrum of as-synthesized particles is amplified by ×4

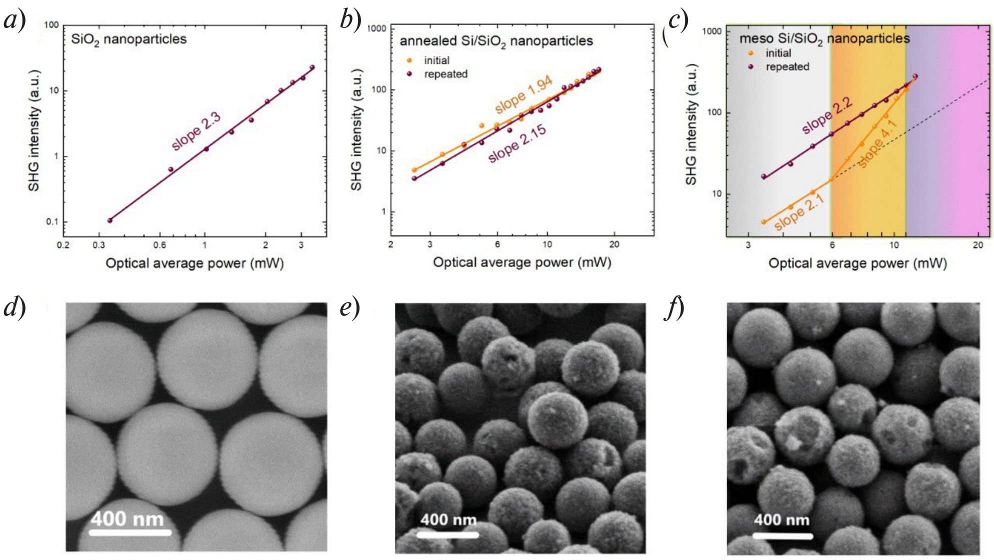

Fig. 2. SHG-to-pump curves for reference SiO_2 NPs (*a*), thermally annealed (*b*) and as-synthesized meso Si/SiO_2 NPs (*c*). The orange curves for (*b*) and (*c*) correspond to initial measurements, purple curves to the repeated measurements. The colored areas in (*c*) represent the following: gray area is the normal SHG response, orange area is an increased slope on SHG response, purple area is the irreversible sample damage. SEM images of SiO_2 (*d*) NPs, annealed (*e*) Si/SiO_2 NPs and meso Si/SiO_2 NPs

The least pronounced SHG signal compared to the reference SiO_2:OH^- NPs was demonstrated by pure meso Si NPs (Fig 2, *a*). A standard slope value of 2 and reproducible SH intensity-pump curves were demonstrated by annealed meso Si/SiO_2 NPs (Fig. 2, *b*), reaching the maximum efficiency in the range of 10–12 mW pump power, that is limited by the material degradation, caused by overheating (the overheat power range is coloured purple in Fig. 2, *c*).

Conclusion

Thus, mesoporous SiO_2 framework of the Si/SiO_2 nanoparticles under consideration plays a double positive role for the nonlinear process: it stabilises the Si material and also the SiO_2:OH^- material itself possesses second-order nonlinearity and influences the observed second harmonic signal.The proposed mesoporous Si/SiO_2 nanoparticles can be considered as a very promising structure for potential applications in optoelectronics, microelectronics and biomedical fields.

Acknowledgments

We thank the N.N. Semenov Federal Research Center for Chemical Physics for providing equipment for measuring second harmonic generation.

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Received 24.07.2024. Approved after reviewing 12.08.2024. Accepted 13.08.2024.