




# Evolution of size distribution of Si nanoparticles produced by pulsed laser ablation in water

A. Krivonosov<sup>1</sup> · D. Zuev<sup>1</sup> · S. Kaputkina<sup>2</sup> · V. Mikhailovskii<sup>2</sup> · E. Egorova<sup>1</sup>  · E. Ageev<sup>1</sup> · G. Odintsova<sup>1</sup>

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## Abstract

In this work, we study ablation of silicon in distilled water under the action of laser pulses with nanosecond duration. The size distribution of produced particles depends on the laser processing parameters and therefore can be modified by the varying distance between laser pulses, laser fluence or pulse duration. The properties of fabricated nanostructures are investigated by scanning electron microscopy to acquire statistical information on nanoparticle sizes. These results can be promising for dielectric nanophotonics, photovoltaics or cancer treatment where relatively large spherical silicon particles are necessary.

**Keywords** Nanoparticles · Silicon nanoparticles · Laser ablation · Size dependence · Fracture

## 1 Introduction

Quantum confinement effect provides a dramatic change in the properties of bulk material compared to nanoparticles (NPs). This change can be manifested in NPs optical, chemical, or other characteristics, motivating a strong demand for various types of nanomaterials and therefore, the fast development of their fabrication techniques.

Silicon is one of the most widespread semiconductor materials in the world, commonly used in the current manufacture of electronic components. Decrease of Si crystal size down to nanoscale results in a significant change of electronic energy bands luminescent properties in the visible and near-infrared (IR) (Takagi et al. 1990) and enhanced absorption in the ultraviolet, visible and IR (Her et al. 1998; Wu et al. 2002). These properties open up numerous

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✉ E. Egorova  
elena1998959@gmail.com

<sup>1</sup> ITMO University, 49 Kronverksky Pr., St. Petersburg, Russia 197101

<sup>2</sup> St. Petersburg State University, 7/9 Universitetskaya nab, St. Petersburg, Russia 199034

promising applications in photonics (optical nanoantennas (Krasnok et al. 2013), detectors (Gonzalez and Veinot 2016) and many others), photovoltaics (Priolo et al. 2014; Wippermann et al. 2016), biology and medicine [drug delivery (Salonen et al. 2008), fluorophores (Gu et al. 2013) and photodynamic therapy (Kovalev and Fujii 2005; Timoshenko et al. 2006)].

In general silicon nanomaterials can be fabricated by chemical, physical, physicochemical, and electrochemical methods [one can find a recent review in (Kabashin et al. 2019)]. Recently laser-assisted methods of Si NPs formation called great attention due to provided chemical purity and ability to control the size, phase state, and morphology of produced nanomaterials. Among them pulsed laser ablation in liquids (PLAL) (Dolgaev et al. 2002; Fojtik and Henglein 1993) is a rather simple method of synthesis (there is no complicated vacuum or chemical equipment) yielding in production of NPs colloidal solution, which can be easily stored, transported or used to develop various functional surfaces (Thompson et al. 2013).

Nanosecond PLAL (Abderrafi et al. 2011) is an attractive method, since strong competitiveness and reliability of available fiber-based laser sources. Generated NPs have a wide distribution of sizes, which can be further tailored through laser-induced fragmentation (Eidelman et al. 2017) or size-selectively optically printed from colloid (Zaza et al. 2019) to fit a particular application.

Very recently, spherical Si nanoparticles with sizes of a few hundred nanometers (100–400 nm) attracted a great interest due to excitation of strong electric and magnetic dipole resonances providing a unique optical response in the visible and near IR ranges (Krasnok et al. 2013). For example, silicon particles with diameter 80–160 nm was proposed for NP antireflective coatings (Baryshnikova et al. 2016). Enhanced emission extraction and selective excitation of NV centers were demonstrated with the silicon nanoparticles with sizes of a few hundred nanometers (Krasnok et al. 2015). Oligomers from silicon nanospheres with an average size of about 100 nm were used to experimentally demonstrate magnetically induced transparency (Yan et al. 2015).

Applied to photovoltaics and energy storage sub-10 nm silicon NPs can enhance conversion efficiency of commercial solar cells (Rasouli et al. 2017); active Si NPs (100–400 nm) material sealed in pores of 3D microporous current collector by graphene layers significantly improves a cycling stability of Li-Ion battery (Shelke et al. 2017). Si particles with sizes in the range from ~40 to ~250 nm in diameter NPs can be of direct interest for solar water heating and vaporization (Ishii et al. 2016).

In medical applications, the laser-ablated Si NPs with a mean size of 25–30 nm in diameter were used to improve the efficiency of radio frequency-based treatment of cancer (Tamarov et al. 2014). PEG-coated laser-synthesized Si NPs (mean size about 25 nm) were conjugated with radioactive  $^{188}\text{Re}$  and used as suitable carriers at nuclear therapy (Petriev et al. 2019).

However, most papers in the formation of Si NPs by nanosecond PLAL devoted to NPs generation with particular size (Rawat et al. 2018; Ulusoy Ghobadi et al. 2016; Vaccaro et al. 2014) and therefore did not consider size dependence on laser processing parameters. Here for nanosecond PLAL, we study the effect of laser fluence, pulse duration and scanning strategy on size of formed Si NPs.

## 2 Materials and methods

Commercially available machine (Minimarker 2) on the base of ytterbium pulsed fiber laser ( $\lambda = 1.06 \mu\text{m}$ ,  $\tau = 4\text{--}200 \text{ ns}$ ,  $f = 10\text{--}99 \text{ kHz}$ , maximum average power  $P_{\text{aver}} = -20 \text{ W}$ ) was used. The laser spot with a focal diameter of  $d_0 = 50 \mu\text{m}$  was moved

over the sample surface with a velocity  $V_{sc}$  from 1 to 8000 mm/s. An experimental design is presented in Fig. 1.

The silicon wafer with sizes of  $7 \times 7 \times 0.25$  mm was used as the target. Samples were ultrasonically washed in distilled water and acetone in sequence. Then cleaned substrate was placed to contamination-free Petrie dish filled with 2 ml of distilled water, where nanosecond PLAL took place. Finally, 50  $\mu$ l of obtained colloidal solution was dropped on silicon substrate dried out under normal conditions for subsequent studies.

The resulting NPs were investigated in an Auriga (Carl Zeiss) scanning electron microscope (SEM) operating at 20 kV. SEM images were analyzed with an open-source software ImageJ (Schneider et al. 2012) to acquire statistical information on NPs sizes.

Laser particle size analyzer SZ100 (Horiba Jobin–Yvon) was used to measure the zeta-potential of colloidal solutions.

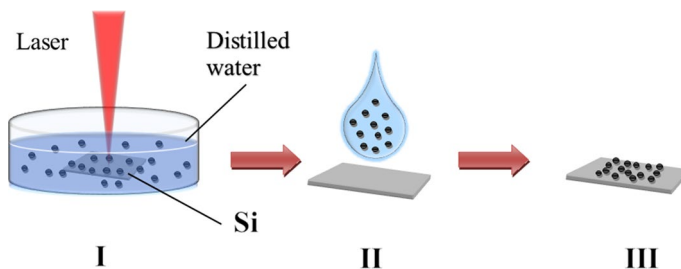
### 3 Results and discussion

#### 3.1 Effect of scanning strategy on NPs size

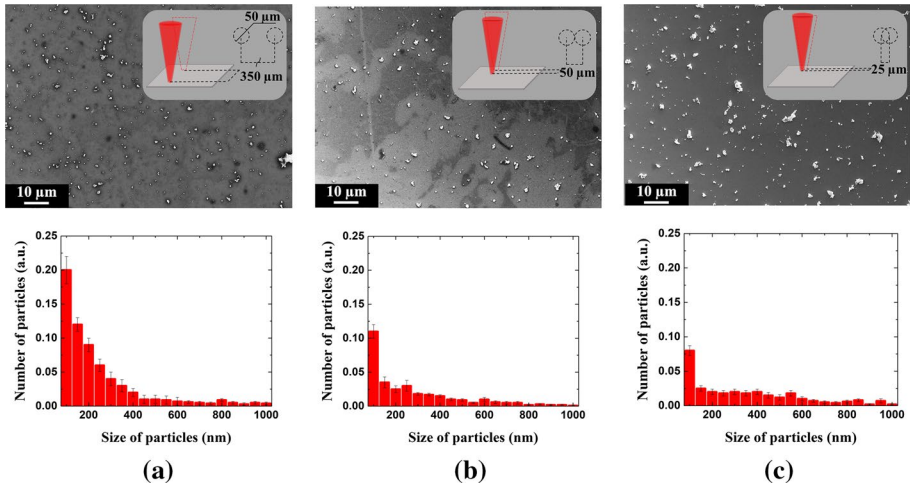
PLAL process is accompanied with cavitation bubble appearance (Tsuji et al. 2004), in the case of nanosecond duration of laser pulses bubble size and lifetime can be up to 200  $\mu$ m and 100–200  $\mu$ s (De Giacomo et al. 2013; Lam et al. 2016), that could have a substantial impact on NPs generation. Three typical cases can be selected: the distance between consecutive laser pulses is higher than cavitation bubble size, laser pulses come one after another immediately (0% overlapping), and 50% pulse overlapping (Fig. 2). For all tests here, pulse duration is 50 ns and fluence is 10 J/cm<sup>2</sup>.

For short distance between pulses or their overlapping laser radiation is partially blocked by growing cavitation bubble, thereby providing additional heating, that results in an enhancement of agglomeration processes in the bubble volume. At the same time, the heating of silicon target decreases due to partial loss of laser power, which has a negative impact on NPs concentration in the solution.

Therefore, the optimal scanning pattern for the generation of NPs with the highest concentration and uniformity of size distribution is that supporting the 350  $\mu$ m distance between laser pulses. This pattern is used at all experiments stated below.



**Fig. 1** A schematic course of the experiment: **I** ablation of Si target by nanosecond laser pulses in distilled water, **II** drop deposition of obtained colloidal solution on silicon substrate, **III** natural drying and preparation for SEM studies



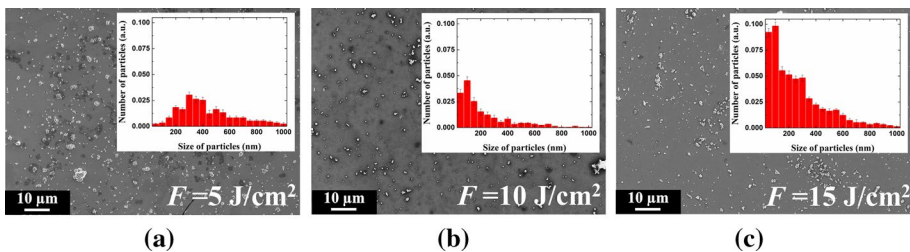
**Fig. 2** SEM images (first row) and size distribution histograms (second row) of Si NPs formed by PLA in water for different distances between laser pulses (*overlapping*): **a** 350 μm (0%), **b** 50 μm (0%) and **c** 25 μm (50%)

### 3.2 Effect of laser fluence (in the range 5–15 J/cm<sup>2</sup>) on NPs size

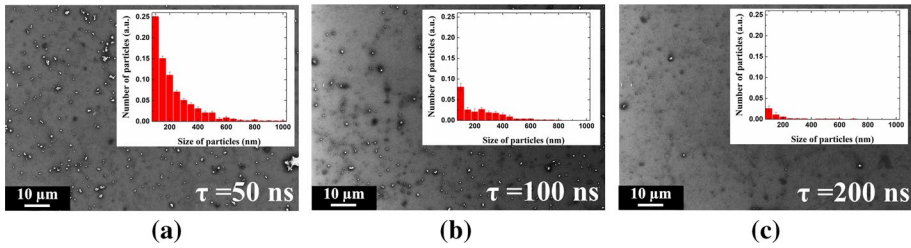
Silicon ablation threshold for 50 ns laser pulses at 1064 nm was experimentally found to be equal to 2 J/cm<sup>2</sup>. Therefore, to ensure intense ablation of a silicon target, the lowest used fluence is 5 J/cm<sup>2</sup>, while upper boundary (15 J/cm<sup>2</sup>) comes from a processing limit of available laser source. Figure 3 presents obtained results. One can see that fluence growth gives considerable increase in NPs concentration, while size distribution is not uniform—both large and small particles can be found. Probably it comes from an enlargement of ablated silicon as the fluence increases.

### 3.3 Effect of laser pulse duration (in the range 50–200 ns on NPs size

To investigate the effect of laser pulse duration on the size of formed NPs all PLAL experiments in this section was made at the fluence of 10 J/cm<sup>2</sup> (Fig. 4).



**Fig. 3** SEM images and size distribution histograms (insets) of Si NPs formed by PLA in the water at different fluences: **a** 5 J/cm<sup>2</sup>, **b** 10 J/cm<sup>2</sup> and **c** 15 J/cm<sup>2</sup>



**Fig. 4** SEM images and size distribution histograms (insets) of Si NPs formed by PLA in the water at different durations of laser pulses: **a** 50 ns, **b** 100 ns and **c** 200 ns

**Table 1** Effect of laser processing parameters on Si NPs size at PLA in water

	Size distribution (nm)
Distance between laser pulses ( $\mu\text{m}$ )	
350	$204 \pm 33$
50	$375 \pm 57$
25	$573 \pm 75$
Laser fluence ( $\text{J}/\text{cm}^2$ )	
5	$226 \pm 40$
10	$164 \pm 21$
15	$500 \pm 117$
Pulse duration (ns)	
50	$210 \pm 45$
100	$132 \pm 32$
200	$126 \pm 10$

In the case of 50 ns laser pulses, silicon reaches higher temperatures than for 100 ns and 200 ns pulses due to faster heating. Therefore, it longer resides in a liquid state after the cavitation bubble collapse, and consequently there is higher probability of agglomeration processes. Potentially, it could provide a quantity reduction for large particles with an increase in laser pulse duration.

To analyze the stability of colloidal solutions, zeta-potential measurements were performed. The typical value is found to be  $-60$  mV, which is indicative of high solution stability and a low tendency for agglomeration. Table 1 summarizes the data of experimental findings.

### 4 Summary

In this work, Si NPs produced by nanosecond PLA in distilled water was investigated. This process allows generation of NPs with a wide distribution of sizes, which can be modified to some extent by altering key laser processing parameters—the distance between laser pulses, laser fluence, and pulse duration.

These results represent the initial step to the fabrication of spherical silicon particles for the benefit of such rapidly developing areas as dielectric nanophotonics, photovoltaics or cancer treatment where relatively large spherical silicon particles are necessary.

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