

INFLUENCE OF THE EXPERIMENTAL PARAMETERS ON SILICON NANOPARTICLES PRODUCED BY LASER ABLATION

C. Grigoriu^{*}, I. Nicolae, V. Ciupina^a, G. Prodan^a, H. Suematsu^b, K. Yatsui^b

National Institute for Laser, Plasma and Radiation Physics, Laser Department,
Atomistilor 409, P.O.Box MG 36, Bucharest-Magurele, Romania

^a“Ovidius” University, Scientific Research Center for Micro and Nanostructures
Mamaia 124, Constanta, 8700, Romania

^bNagaoka University of Technology, Extreme Energy-Density Research Institute,
Nagaoka, Niigata, 944-2188, Japan

Influence of the laser wavelength, fluence, gas and gas pressure on silicon nanoparticles produced by laser ablation is reported. Nanoparticles ranging from 2 nm to 13 nm were generated by ablation of silicon target into He or Ar, (250-550 mbar) with a Nd:YAG laser, (335 and 532 nm, 5 ns), at a fluence of 4-8 J/cm². The shape, structure, and size distribution were determined by transmission electron microscopy. 90% of nanoparticles were in the range 2-10 nm, regardless pressure, wavelength or fluence. The wavelength 355 nm and higher fluence, 8 J/cm², are more suitable for smaller nanoparticle synthesis (2-5 nm). The optimal conditions for an efficient synthesis of minimum sized silicon nanoparticles were 355 nm / 8 J/cm² / 550 mbar / He.

(Received April 21, 2004; accepted June 22, 2004)

Keywords: Laser ablation, Silicon nanoparticles, Primary particle size

1. Introduction

The recent literature reveals a considerable interest in the nanoparticle field. The theoretical understanding of the nanoparticle structure and related characteristics are very important aspects to engineer properties and functionalities for new applications heretofore unavailable in conventional materials. Nanoparticle structure, size distribution, monodispersity, composition, stability, agglomeration, photoluminescence, scale up production, are numerous challenging problems for the scientific community.

Silicon nanocrystals, have raised hopes in applications for Si-based devices. A substantial interest has received the development of numerous synthesis techniques. Among them much attention has been paid recently to the study and developing of pulsed laser ablation (PLA). A great deal of work has been carried out to produce silicon nanoparticles by PLA, to control their size, crystallinity, luminescence (quantum dots), selective adsorption property etc.[1-31].

Generally, synthesis of silicon nanoparticles by PLA technique is made in an ambient gas as argon, helium; the nanoparticles are collected on a filter, substrate, cold plate, electron microscope grid, etc. Usually in most of the works the ambient pressure is in the range 0.1- 13 mbar excepting the works of M.S. El-Shall et al [3,7,8,16-18,22,28] in which the pressure was 1000-1300 mbar.

The main goal of our work is to optimize the PLA method so that the synthesis of silicon/silicon-rich silicon oxide nanopowders to have a high efficiency.

Here we report the investigations on synthesis by PLA of silicon nanopowder with the aim to reveal the role of the laser wavelength, fluence, gas and pressure on nanoparticle morphology and size distribution. The experiments have been done at a pressure of 250-550 mbar, higher than in the

* Corresponding author: grigoriu@ifin.nipne.ro

standard methods. The silicon nanopowders and individual nanoparticles were examined by transmission electron microscopy.

2. Experimental

The method and apparatus for nanopowder synthesis have been reported elsewhere [32, 33]. The experimental setup consisted of a stainless steel chamber, with target system, gas handling, focusing lens and collector. The silicon target was almost uniformly irradiated due to the combined rotation-translation movement of the target. The experiments were conducted in flowing argon and helium (1 l/min flow rate, 99.99% purity). Initially the chamber was evacuated by a turbo molecular pump at a base pressure of 4×10^{-6} mbar. In our case, the gas-suspended nanoparticles were collected on Millipore filters (pore size 100 nm) after 36,000 laser shots.

The Nd:YAG laser, model Surelite II-10, delivers pulses at the wavelength of 532 nm (second harmonic) and 355 nm (third harmonic) with the duration of 5 ns, and repetition rate of 10 Hz. The fluences have been in the range of 4-8 J/cm².

The transmission electron microscope (TEM) was Phillips, model CM 120, and JEOL JEM-2000FXII operating at an accelerating voltage of 200 kV; as grids we utilized formvar and formvar/carbon coated 300 mesh copper grids.

The powder was deposited on the grid by lightly direct touching of the nanopowder. We consider this technique as real random sampling. The measurements have been made after 3 months aging in ambient atmosphere, at room temperature, without any special precautions.

3. Results and discussion

The silicon nanoparticles collected on the filter are yellow, light orange, in color [7].

The figure 1 shows a typical TEM image of clusters with particles having diameters in the range 3-14 nm. From TEM images it is evidently that the particles stick together in clusters of more or less complicated shape following of a collision-coalescence process and cluster-cluster aggregation.

We have to emphasise difficulties created by the electron beam induced heating of the Si individual nanoparticle or clusters. This phenomenon in most cases leads to melting and evaporation of the sample.

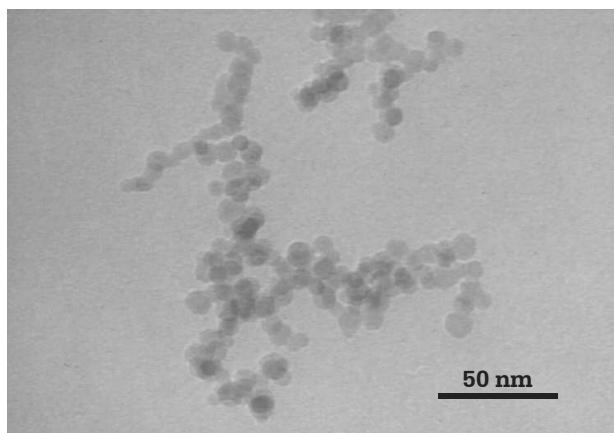


Fig. 1. TEM image of typical cluster; Experimental conditions: $\lambda=355$ nm / 4 J/cm² / helium / 400 mbar.

In Fig. 2, such nanoparticles having diameter of ~10 nm are shown. The nanoparticles look almost spherical. Figure 2a presents the image of a single particle; in Fig. 2b, the structure is more

visible: a silicon core coated with an amorphous layer [1,18,19,26]. Kanemitsu and Makimura et al. [1,5] analyzing similar samples by x-ray photoemission spectroscopy and Fourier-transform infrared spectroscopy, confirmed that the outlayer is amorphous silicon oxide. The silicon dioxide layer was formed either due to some residual oxygen in the experimental chamber or when was taken out of the chamber. All images have shown that the oxide coating (thickness 1.2-1.5 nm) is at most weakly dependent on the diameter.

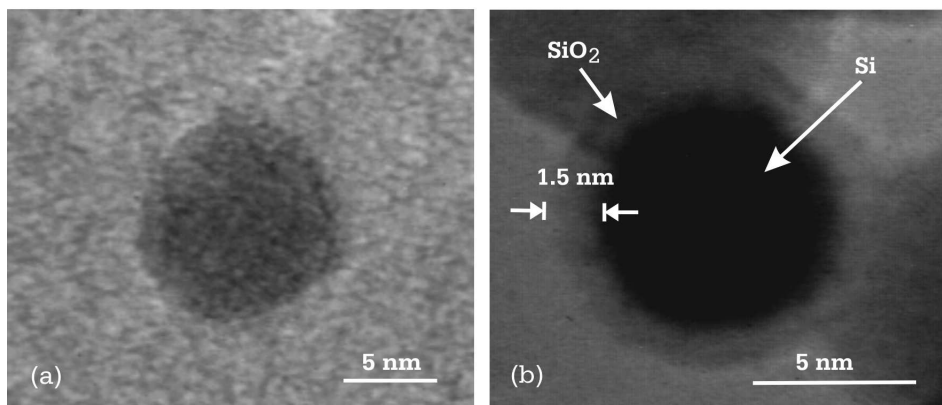


Fig. 2. TEM image of (a) single nanoparticle obtained in argon / 400 mbar / 355 nm wavelength / 4 J/cm² fluence; (b) particles obtained in argon / 550 mbar / 355 nm wavelength / 4 J/cm² fluence.

The selected area electron diffraction patterns from clusters of Si nanoparticles, showed that in many cases the particles are crystalline. For example in Fig. 3 is illustrated the pattern for a powder created in helium at 400 mbar, λ=355 nm, fluence 4J/cm². It should be noted that only typical rings of the crystalline silicon appear, they being attributed to the silicon core [1,2,19,26]. Diffraction lines due to oxides were not found; this also suggests that SiO₂ coating is amorphous.

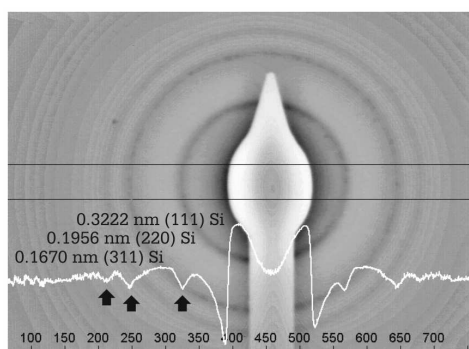


Fig. 3. Selected-area electron diffraction pattern of nanoparticles prepared in helium at 400 mbar / laser wavelength 355 nm / 4 J/cm² fluence.

Fig. 4 shows high resolution TEM images, illustrative for the interplanar spacing. The properties of the Si are similar to those observed by [19, 26]. It is observed a lattice fringe image spacing of 0.316 (a) or 0.319 nm (b), corresponding to the (111) planes of the diamond structure. Our investigations on most of the samples consisting of single crystal domains showed lattice constants in the range 0.310 - 0.329 nm (111), 0.193-0.202 (220), 0.160-169 (311). Once again we have to mention that not all particles showed lattice patterns, but amorphous-like structure.

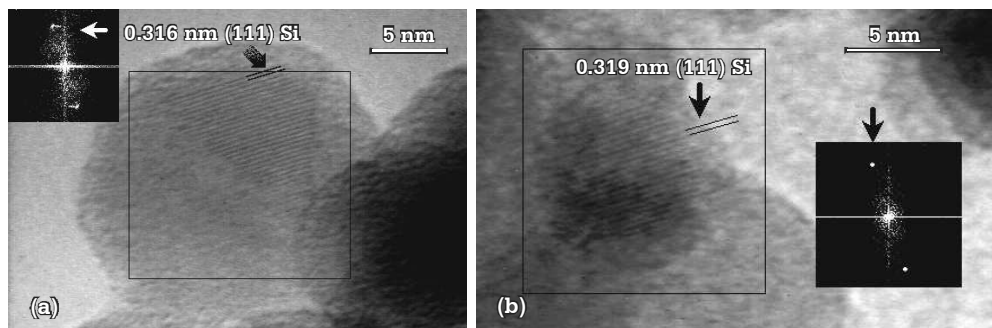


Fig. 4. High resolution transmission electron microscope image of a silicon/silicon-rich silicon oxide nanoparticle: (a) 355 nm wavelength / argon / 550 mbar / 8 J/cm² fluence, (left side, Fourier transform); (b) 355 nm wavelength / argon / 400 mbar / 4 J/cm² fluence, (right side, Fourier transform); The lattice pattern indicative of (111) planes of diamond structure.

One of the goals of our work was the study of the influence of the experimental parameters on the size distribution. Our interest was to determine the optimal conditions for an efficient synthesis of minimum sized silicon nanoparticles (related to applications as quantum dots).

First of all we have to mention that due to clustering there are some uncertainties that clearly make the evaluation of the size distribution troublesome. The evaluation was not regarded as very accurate for the careful size distribution.

Figure 5 shows the size histograms of the powders obtained at different laser wavelengths, fluences, gas pressure, in helium or argon. As one can see, the statistical distribution has an asymmetric shape with a tail toward larger diameters. It was seen that in many cases, in spite of a slight uncertainty, best fit has been achieved with log-normal distribution function [1,34].

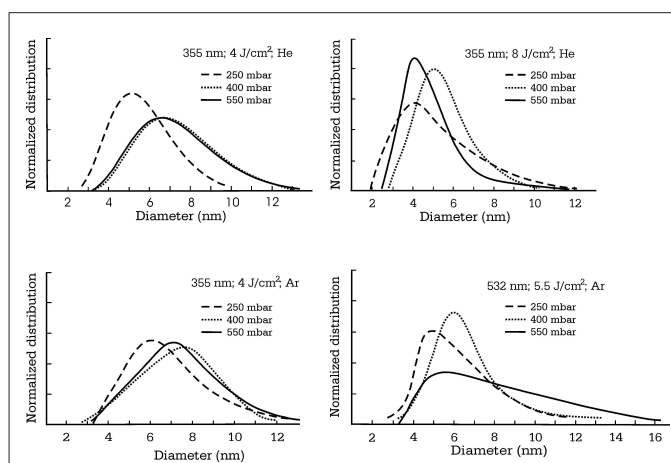


Fig. 5. Size distribution for silicon nanoparticles produced in different experimental conditions.

Table 1 summarizes the mean sizes of the primary particles, and the percentage of particles having the size of 2-5 nm and 2-10 nm.

It is noted that in most cases almost 90% of nanoparticles are in the range 2-10 nm, regardless of pressure, wavelength or fluence.

At the same time, one can see that the percentage of the particles with size in the range 2-5 nm is much diminished, ~9-64 %, the best situation being at $\lambda=355$ nm, in helium. It is worth pointing out that the particles synthesized in helium, with laser pulses $\lambda=355$ nm, fluence 8 J/cm², have the smallest arithmetic average diameter, around 5 nm and 64% of them are in the range 2-5 nm. The most likely explanation is that the irradiation of the silicon target with higher fluences

results in formation of silicon atoms with higher charges and kinetic energy expanding into a larger region, hence their density becomes lower, and consequently smaller particles appear.

Some authors Kanemitsu et al [1], Makimura et al [5], reported a diameter dependence on gas pressure. In their case, for the pressure was 0.5-10 Torr (the other parameters being similar to ours) the larger particles are formed at higher inert-gas pressure. In our experimental conditions, particularly pressure of 250-550 mbar, we could not draw a clear conclusion on the size-pressure dependence. In our opinion this can be explained by two factors: (a) ablation process in gases at a pressure of 250-550 mbar is much more complicated, (b) difficulties on an accurate evaluation of the particle size.

Concerning the gas influence we found that in argon the particles have larger diameters than in helium.

Table 1.

λ [nm]	Fluence [J/cm^2]	Gas	Pressure [mbar]	Particles with diameter in the range 2-5 nm [%]	Particles with diameter in the range 2-10 nm [%]	Arithmetic mean diameter [nm]	The diameter for which the distribution function is maximum [nm]
355	4	He	250	38.2	100	5.7	5.2
			400	9.3	89.2	7.5	6.8
			550	11.4	90.1	7.4	6.6
355	8	He	250	57.3	98.1	5.1	4.0
			400	38.5	99.8	5.6	5.2
			550	63.9	98.8	4.9	4.0
355	4	Ar	250	17.2	92.5	6.9	6.0
			400	12.5	93.9	7.3	7.6
			550	43.2	89.6	7.4	7.2
532	5.5	Ar	250	29.4	94.9	6.3	5.0
			400	15.9	97.5	6.3	6.0
			550	15.2	73.6	8.2	5.6

4. Conclusions

In summary, Si/SiO₂ particles were produced by laser ablation (UV and Vis. wavelength, 4-8 J/cm², in Ar and He). The main conclusions of our work are as follows:

- The experiments have been carried out in the range of the gas pressure of 250-550 mbar, (different than the usual range reported in the literature, 0.1-13 mbar or 100-1300 mbar);
- 90% of nanoparticles are in the range 2-10 nm, regardless pressure, wavelength or fluence.
- 9.3-63.9 % of nanoparticles are in the range 2-5 nm, depending upon wavelength, gas and pressure;
- The particles synthesized in argon are larger than in helium;
- The wavelength 355 nm and higher fluence, 8 J/cm², are more suitable for smaller nanoparticle synthesis (2-5 nm);
- The optimal conditions for an efficient synthesis of minimum sized silicon nanoparticles are: 355 nm / 8 J/cm² / 550 mbar / He.

References

- [1] Y. Kanemitsu, *Phys. Rev. B* **48**, 4883 (1993).
- [2] E. Werwa, A. A. Seraphin, L. A. Chiu, C. Zhou, K. D. Kolenbrander, *Appl. Phys. Lett.* **64**, 1821 (1994).
- [3] M. S. El-Shall, S. Li, T. Turkki, D. Graiver, U. C. Pernisz, M. I. Baraton, *J. Physical Chemistry*, **99**, 17805 (1995).
- [4] Y. Yamada, T. Orii, I. Umezu, S. Takeyama, T. Yoshida, *Jpn. J. Appl. Phys.* **35**, part1, 1361 (1996).
- [5] T. Makimura, Y. Kunii, K. Murakami, *Jpn. J. Appl. Phys.* **35**, part 1, 4780 (1996).
- [6] A. A. Seraphin, E. Werwa, K. D. Kolenbrander, *J. of Materials Research* **12**, 3386 (1997).
- [7] S. Li, M. S. El-Shall, *Appl. Surface Science* **127-129**, 330 (1998).
- [8] S. Li, I. N. Germanenko, M. S. El-Shall, *J. Phys. Chem. B* **102**, 7319, (1998).
- [9] D. B. Geohegan, A. A. Poretzky, G. Dusher, S. J. Pennycook, *Appl. Phys. Lett.* **72**, 2987 (1998).
- [10] D. B. Geohegan, A. A. Purtzki, G. Dusher, S. J. Pennycook, *Applied Phys. Letters* **73**, 438 (1998).
- [11] T. Makimura, Y. Kunii, N. Ono, K. Murakami, *Applied Surface Science* **129**, 388 (1998).
- [12] D. H. Lowndes, C. M. Rouleau, T. Thundat, G. Duscher, E. A. Kenik, S. J. Pennycook, *Applied Surface Science* **129**, 355 (1998).
- [13] D. H. Lowndes, C. M. Rouleau, T. Thundat, G. Duscher, E. A. Kenik, S. J. Pennycook, *J. Materials Research* **14**, 359 (1999).
- [14] T. Makino, N. Suzuki, Y. Yamada, T. Yoshida, T. Seto, N. Aya, *Appl. Phys. A – Materials Science & Processing* **69**, S243 (1999).
- [15] T. Makino, N. Suzuki, Y. Yamada, T. Yoshida, T. Seto, N. Aya, *Appl. Phys. A – Materials Science & Processing*, **69**, S243 (1999).
- [16] S. Li, I. N. Germanenko, M. S. El-Shall, *Journal of Cluster Science* **10**, 533 (1999).
- [17] I. N. Germanenko, S. Li, S. J. Silvers, M. S. El-Shall, *Nanostructured Materials* **12**, 731 (1999).
- [18] J. A. Carlisle, M. Ogol, I. N. Germaneko, Y. B. Pithawalla, M. S. El-Shall, *Chem. Phys. Lett.* **326**, 335 (2000).
- [19] M. Hirasawa, T. Seto, N. Aya, *J. of Nanoscience and Nanotechnology* **1**, 381 (2001).
- [20] T. Seto, Y. Kawakami, N. Suzuki, M. Hirasawa, N. Aya, *Nano Letters* **1**, 315 (2001).
- [21] K. Hata, M. Fujita, S. Yoshida, S. Yasuda, T. Makimura, K. Murakami, H. Shigekawa, W. Mizutani, H. Takumoto, *Appl. Phys. Lett.* **79**, 692 (2001).
- [22] I. N. Germaneko, S. Li, M. S. El-Shall, *J. Phys. Chem. B* **105**, 59 (2001).
- [23] M. Inada, H. Nakagawa, I. Umeza, A. Sugimura, *Appl. Surface Science* **197**, 666 (2002).
- [24] T. Makimura, T. Mizuta, K. Murakami, *Japanese J. Appl. Phys., Part 2 Letters* **41(2A)** L144 (2002).
- [25] M. Ullmann, S. K. Friedlander, A. Schmidt-Ott, *J. Nanoparticle Research* **4**, 499 (2002).
- [26] T. Orii, M. Hirasawa, T. Seto, *Appl. Phys. Lett.* **83**, 3395 (2003).
- [27] M. Inada, I. Umeza, A. Sugimura, *J. Vacuum Science & Technology A*, **21**, 84 (2003).
- [28] M. S. El-Shal, V. Abdelsayed, Y. B. Pithawall, E. Alsharaeh, *J. Phys. Chem. B* **107**, 2882 (2003).
- [29] M. Inada, H. Nakagawa, I. Umezu, A. Sugimura, *Materials Science and Engineering B-Solid State Materials for Advanced Technology* **101**, 283 (2003).
- [30] T. Orii, M. Hirasawa, T. Seto, N. Aya, S. Onari, *Eur. Phys. J. D* **24**, 119 (2003).
- [31] V. Narayanan, R. K. Thareja, *Applied Surface Science* **222**, 382 (2004).
- [32] K. Yatsui, T. Yukawa, C. Grigoriu, M. Hirai, W. Jiang, *J. Nanoparticle Research* **2**, 75 (2000).
- [33] C. Grigoriu, M. Hirai, K. Nishiura, W. Jiang, K. Yatsui, *J American Ceram. Soc.* **83**, 2631 (2000).
- [34] C. G. Granqvist, R. A. Buhrman, *J. Appl. Phys.* **47**, 2200 (1976).