

論文 / 著書情報  
Article / Book Information

|           |                                                                                                                                                            |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Title     | The Effect of Energy Density on Yield of Silicon Nanoparticles Prepared by Pulsed Laser Ablation in Liquid                                                 |
| Authors   | Pattarin Chewchinda, Osamu Odawara, Hiroyuki Wada                                                                                                          |
| Citation  | Applied Physics A, Volume 117, 1, pp. 131–135                                                                                                              |
| Pub. date | 2014, 2                                                                                                                                                    |
| Note      | The final publication is available at Springer via <a href="http://dx.doi.org/10.1007/s00339-014-8293-7">http://dx.doi.org/10.1007/s00339-014-8293-7</a> . |

## The Effect of Energy Density on Yield of Silicon Nanoparticles Prepared by Pulsed Laser Ablation in Liquid

P. Chewchinda, O. Odawara, H. Wada

*Department of Innovative and Engineered Materials, Tokyo Institute of Technology*

*4259-J2-41 Nagatsuta-chou, Midori-ku, Yokohama-shi, Kanagawa-ken 226-8503*

*Email: chewchinda.p.aa@m.titech.ac.jp*

*Tel: (+81)-45-924-5567, Fax: (+81)-45-924-5567*

### Abstract

The effect of energy density on the yield of silicon nanoparticles was studied. Silicon nanoparticles were prepared by laser ablation in ethanol. The yield of nanoparticles was calculated and its results indicate that high energy density led to more nanoparticles production. Particle size was also affected by varying energy density. From TEM images, higher energy density resulted in smaller nanoparticles, which can be explained by nucleation and growth theory. Photoluminescence spectra revealed blue shift of emission peak at high energy density supporting TEM results. Silicon peak was detected by EDS analysis along with oxygen. This means oxidation of silicon might occur within the sample.

**Keywords:** laser ablation, silicon, nanoparticles, ethanol, energy density

This is an author –created, un-copied version of an article accepted for publication in Applied Physics A. The publisher is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The Version of Record is available online at 10.1007/s00339-014-8293-7.

## 1. Introduction

Silicon nanoparticles have been employed into diverse applications since they are abundant, environmentally friendly, and cheap [1-5]. In biological field, silicon nanoparticles can be utilized as fluorescent imaging agent. Compared to conventional organic dyes, silicon nanoparticles are more stable against photobleaching and metabolic degradation. In addition, emission spectra can be controlled by tuning size of nanoparticles [6-10]. It was reported that silicon nanoparticles were successfully utilized as fluorescent agents for both *in vivo* and *in vitro* images with no apparent toxicity [11-13]. Another report suggested an application of these particles in drug delivery system. According to this study, silicon nanoparticles revealed high resistance to biodegradability, high payload, and multivalent loading ability [14]. These previous literature emphasize the importance of silicon nanoparticles in biological application.

Photovoltaic device is another interesting application for silicon nanoparticles. After multiple exciton generation (MEG) was proved to occur in silicon quantum dot, it created new possibilities for improving conversion efficiency of solar cell [15-16]. Under this condition, the excess energy absorbed at short wavelength can generate more than one exciton. It was shown that the current density and the conversion efficiency of solar cell with silicon nanoparticles were

increased compared with the device without these particles [17-18]. With suitable electrolyte concentration, the device performance can be enhanced even further [19]. Although this technology is still in development, these previous work already proved that silicon nanoparticles play a role in improving the performance of solar cell.

To prepare silicon nanoparticles, several techniques have been proposed. These include laser pyrolysis [11-12, 20-21], electrochemical etching [5, 22-23], and laser deposition [24-25]. Unfortunately, these methods either result in impure product or suffer from complicated experimental system.

Recently, laser ablation in liquid technique has been proposed. With this process, silicon nanoparticles can be prepared with high purity and the experimental setup is also simple [26-28]. However, several parameters can affect the properties of the obtained silicon nanoparticles such as liquid media, laser wavelength, and laser fluence [26, 29-31]. In this work, energy density of laser irradiation was varied and its effects on silicon nanoparticles were studied.

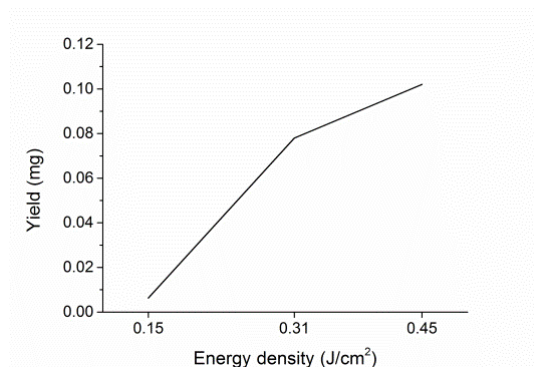
## 2. Experiment

P-type silicon wafer (crystal orientation <100>, resistivity 11.5-15.5  $\Omega$ -cm, thickness 600  $\mu$ m) was used as a target and weighed by microbalance. This target was then immersed in 40 mL of 99.5% ethanol and irradiated with Q-switch Nd:YAG laser at

second harmonic generation ( $\lambda = 532$  nm, pulse width 13 ns, repetition rate 10 Hz). Energy density was varied from 0.15 to 0.45 J/cm<sup>2</sup>. Magnetic stirrer was also utilized in this experiment. After 30 minutes, silicon wafer was weighed again. The yield of nanoparticles was calculated by the difference between weight before and after irradiation of silicon target. The obtained colloidal solution was dropped on copper grid and prepared for TEM and also EDS observation. Photoluminescence (PL) spectra were observed by fluorescence spectrophotometer with excitation wavelength of 350 nm.

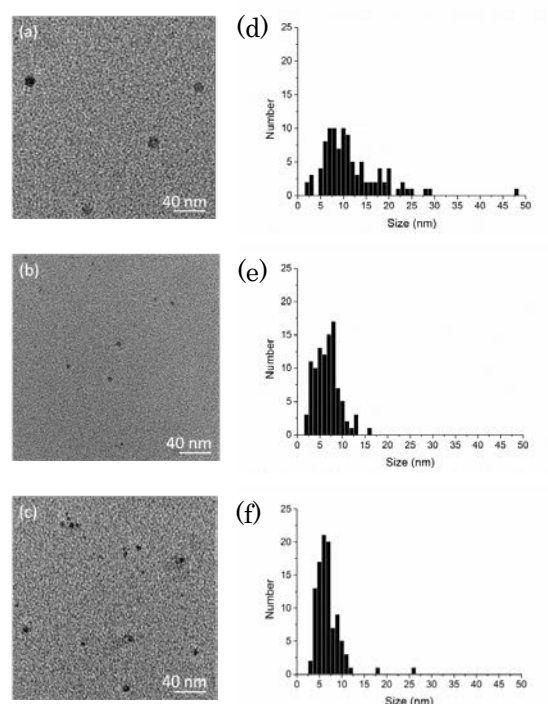
### 3. Results and Discussion

Fig. 1 shows the relation between yield of nanoparticles and energy density of laser irradiation. As energy density increased from 0.15 to 0.31 J/cm<sup>2</sup>, the yield of nanoparticles increased dramatically from 0.01 to 0.08 mg. However, as energy density enhanced further to 0.45 J/cm<sup>2</sup>, it gave rise to only 0.02 mg increase in nanoparticles production



**Fig. 1** Silicon nanoparticles production at each energy density

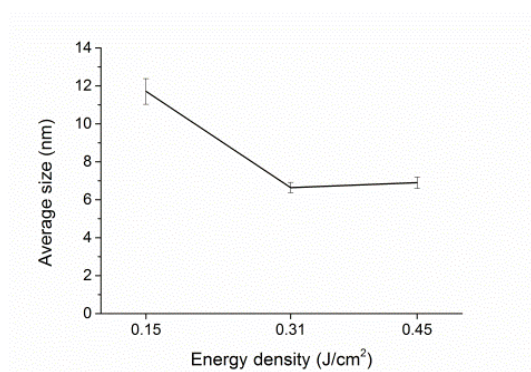
From TEM images, as shown in Fig. 2(a) to 2(c), prepared silicon nanoparticles revealed spherical shape and well dispersed at any energy density. With these images, size distributions were constructed by measuring diameter of 100 nanoparticles. The results are shown in Fig. 2(d) to 2(f). The average size at each energy density was plotted in Fig. 3. From these results, as energy density enhanced, the average size of prepared nanoparticles became smaller. However, as energy density increased beyond 0.31 J/cm<sup>2</sup>, the size was unchanged.



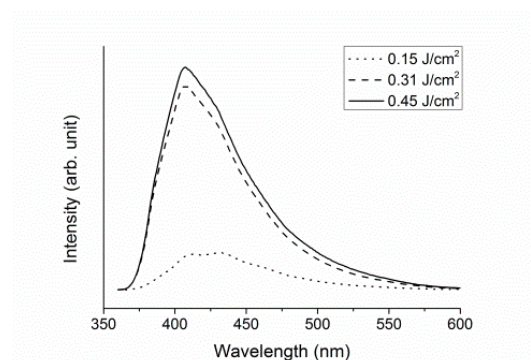
**Fig. 2** TEM images and size distributions of nanoparticles prepared at (a, d) 0.15 (b, e) 0.31 and (c, f) 0.45 J/cm<sup>2</sup>

Photoluminescence is another important property for the study of nanoparticles. From Fig. 4, as energy density increased from 0.15 to 0.31 J/cm<sup>2</sup>,

the emission peak was shifted to lower wavelength. This blue-shifted peak indicates that smaller nanoparticles were prepared at higher energy density [32-34]. For nanoparticles obtained at energy density of  $0.45 \text{ J/cm}^2$ , the peak position appeared to be the same as the one at energy density of  $0.31 \text{ J/cm}^2$  suggesting similar particle size.



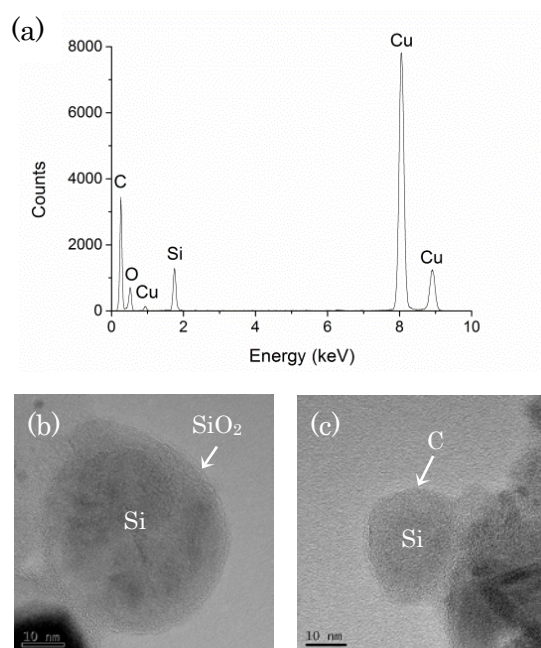
**Fig. 3** Average size of nanoparticles at each energy density



**Fig. 4** PL spectra of nanoparticles prepared at energy density of  $0.15$  (dotted line),  $0.31$  (dashed line), and  $0.45 \text{ J/cm}^2$  (solid line)

To study the composition of nanoparticles, EDS spectroscopy was employed. From the result shown in Fig. 5(a), silicon was detected along with oxygen peak. This means silicon might be oxidized within the sample, which was confirmed by

HRTEM result shown in Fig. 5(b). Copper and carbon peaks generally come from sample grid used during analysis. However, small trace of carbon-coated silicon nanoparticle was observed as shown in Fig. 5(c). In previous literatures, during laser ablation, it is possible that ethanol was decomposed into carbon atoms and interacted with silicon clusters. This process led to the formation of SiC particles [35-36]. In our case, carbon was deposited on silicon nanoparticles instead. This difference possibly comes from the differences in experimental condition, which requires further investigation.



**Fig. 5** (a) EDS spectrum of nanoparticles prepared at energy density of  $0.31 \text{ J/cm}^2$  (b) HRTEM of oxide-coated and (c) carbon-coated silicon nanoparticles

To study the effect of energy density on the yield of nanoparticles, optical absorption heat was brought into

consideration. Optical absorption heat is directly proportional to power density of irradiation based on the following equation

$$H_A = \alpha I_{opt} \quad (1)$$

where  $H_A$  is optical absorption heat,  $\alpha$  is absorption coefficient, and  $I_{opt}$  is power density [37]. Higher optical absorption heat provides more energy for particles generation. As a consequence, higher production yield was obtained at higher energy density. However, as energy density enhanced further, the yield of nanoparticles only increased slightly. One possible explanation is that as the number of nanoparticles increased, the absorption of nanoparticles themselves inhibited the ablation on silicon target. As the ablation decreased, nanoparticles production also declined.

Nucleation will occur only when the concentration reached the supersaturation limit [38]. At low energy density, there are few silicon atoms in plasma plume. Under this condition, it is difficult to reach the supersaturation limit and consequently, nucleation is difficult to occur. Thus, only small number of nuclei was created. During the growth process, silicon atoms attached to nuclei until all surrounding atoms were consumed. These atoms had limited nucleation sites to bind to; therefore, the nuclei grew rapidly leading to large particle size [26, 31]. At higher energy density, the situation reversed. Because of high concentration, supersaturation limit can be reached easily

and nucleation occurred simultaneously. Large number of nuclei was created and they grew gradually. As a result, the final particle size was smaller than that obtained at low energy density. In addition, the previously formed nanoparticles could absorb laser energy which resulted in fragmentation. This process also led to small particle at high energy density.

#### 4. Conclusions

Laser ablation in liquid was employed to prepare silicon nanoparticles at different energy density. Higher energy density resulted in higher nanoparticles production. However, as energy density enhanced further, self-absorption of nanoparticles played a role in inhibiting the ablation on silicon target. Nucleation and growth theory can be used to explain the reason for the size difference. At low energy density, nucleation was difficult resulting in small number of nuclei and large particle size. At high energy density, nucleation occurred simultaneously leading to large number of nuclei and small particle size.

#### Acknowledgment

We would like to thank Prof. Kazutaka Nakamura (Nd:YAG laser), Prof. Takeo Yamaguchi, and Mr. Teruaki Fuchigami (TEM) from Tokyo Institute of Technology for their contribution to this research. This work was supported by the Materials and Structure Laboratory (Tokyo Tech.

collaborative research), JSPS KAKENHI, and NEC C&C Foundation.

## References

- [1] Z. Kang, Y. Liu, S.-T. Lee, *Nanoscale* 3, 777 (2011)
- [2] N. Shirahata, D. Hirakawa, Y. Sakka, *Green Chem.* 12, 2139 (2010)
- [3] W. L. Liong, S. Sreekantan, S. D. Hutagalung, *Proc. of SPIE* 7743, 774306 (2010)
- [4] V. Švrček, D. Mariotti, R. Hailstone, H. Fujiwara, M. Kondo, *Mater. Res. Soc. Symp. Proc.* 1066, (2008)
- [5] V. Švrček, *Nano-Micro Lett.* 1, 40 (2010)
- [6] V. Maurice, O. Sublemontier, N. Herlin-boime, E. Doris, O. Raccurt, *AIP Conf. Proc.* 1275, 44 (2010)
- [7] R. E. Bailey, A. M. Smith, S. Nie, *Physica E* 25, 1 (2004)
- [8] M. Rosso-Vasic, E. Spruijt, Z. Popović, K. Overgaag, B. van Lagen, B. Grandidier, D. Vanmaekelbergh, D. Domínguez-Gutiérrez, L. De Cola, H. Zuilhof, *J. Mater. Chem.* 19, 5926 (2009)
- [9] P. Sharma, S. Brown, G. Walter, S. Santra, B. Moudgil, *Adv. Colloid Interf.* 123–126, 471 (2006)
- [10] M. L. Brongersma, a. Polman, K. S. Min, E. Boer, T. Tambo, H. A. Atwater, *Appl. Phys. Lett.* 72, 2577 (1998)
- [11] F. Erogbogbo, K. Yong, I. Roy, G. Xu, P. N. Prasad, M. T. Swihart, *ACS Nano* 2, 873 (2008)
- [12] F. Erogbogbo, K.-T. Yong, I. Roy, R. Hu, W.-C. Law, W. Zhao, H. Ding, F. Wu, R. Kumar, M. T. Swihart, P. N. Prasad, *ACS nano* 5, 413 (2011)
- [13] J. H. Warner, A. Hoshino, K. Yamamoto, R. D. Tilley, *Angew. Chem.-Ger. Edit.* 44, 4550 (2005)
- [14] F. De Angelis, A. Pujia, C. Falcone, E. Iaccino, C. Palmieri, C. Liberale, F. Mecarini, P. Candeloro, L. Luberto, A. de Laurentiis, G. Das, G. Scala, E. Di Fabrizio, *Nanoscale* 2, 2230 (2010)
- [15] M. C. Beard, K. P. Knutsen, P. Yu, J. M. Luther, Q. Song, W. K. Metzger, R. J. Ellingson, A. J. Nozik, *Nano Lett.* 7, 2506 (2007)
- [16] A. J. Nozik, *Chem. Phys. Lett.* 457, 3 (2008)
- [17] Y. Kawashima, K. Nakaharu, H. Sato, G. Uchida, K. Koga, M. Shiratani, M. Kondo, *Trans. Mater. Res. Soc. Jpn.* 35, 597 (2010)
- [18] G. Uchida, Y. Kawashima, K. Yamamoto, M. Sato, K. Nakahara, T. Matsunaga, D. Yamashita, H. Matsuzaki, K. Kamataki, N. Itagaki, K. Koga, M. Kondo, M. Shiratani, *Phys. Status Solidi C* 8, 3021 (2011)
- [19] H. Seo, Y. Wang, G. Uchida, K. Kamataki, N. Itagaki, K. Koga, M. Shiratani, *Electrochim. Acta* 95, 43 (2013)
- [20] X. Li, Y. He, M. T. Swihart, *Langmuir* 20, 4720 (2004)
- [21] S. Botti, R. Coppola, F. Gourbilleau, R. Rizk, *J. Appl. Phys.* 88, 3396 (2000)
- [22] P. Caregnato, M. L. Dell'arciprete, M. C. Gonzalez, *Photoch. Photobio. Sci.* 12, 1658 (2013)

- [23] V. Švrček, H. Fujiwara, M. Kondo, *Sol. Energ. Mat. Sol. C* 93, 774 (2009)
- [24] X. Y. Chen, Y. F. Lu, Y. H. Wu, B. J. Cho, M. H. Liu, D. Y. Dai, W. D. Song, *J. Appl. Phys.* 93, 6311 (2003)
- [25] D. Riabinina, C. Durand, M. Chaker, F. Rosei, *Appl. Phys. Lett.* 88, 073105 (2006)
- [26] S. Yang, W. Cai, H. Zhang, X. Xu, H. Zeng, *J. Phys. Chem. C* 113, 19091 (2009)
- [27] V. Švrček, M. Kondo, K. Kalia, D. Mariotti, *Chem. Phys. Lett.* 478, 224 (2009)
- [28] D. Rioux, M. Laferrière, A. Douplik, D. Shah, L. Lilge, A. V Kabashin, M. M. Meunier, *J. Biomed. Opt.* 14, 021010 (2009)
- [29] V. Švrček, T. Sasaki, Y. Shimizu, N. Koshizaki, *Appl. Phys. Lett.* 89, 213113 (2006)
- [30] P. a. Perminov, I. O. Dzhun, a. a. Ezhov, S. V. Zaboltnov, L. a. Golovan, G. D. Ivlev, E. I. Gatskevich, V. L. Malevich, P. K. Kashkarov, *Laser Phys.* 21, 801 (2011)
- [31] P. Chewchinda, T. Tsuke, H. Funakubo, O. Odawara, H. Wada, *Jpn. J. Appl. Phys.* 52, 025001 (2013)
- [32] H. Takagi, H. Ogawa, Y. Yamazaki, a. Ishizaki, T. Nakagiri, *Appl. Phys. Lett.* 56, 2379 (1990)
- [33] G. Ledoux, O. Guillois, D. Porterat, C. Reynaud, *Phys. Rev. B* 62, 15942 (2000)
- [34] G. Ledoux, J. Gong, F. Huisken, O. Guillois, C. Reynaud, *Appl. Phys. Lett.* 80, 4834 (2002)
- [35] S. Yang, W. Cai, H. Zeng, X. Xu, *J. Mater. Chem.* 19, 7119 (2009)
- [36] P. G. Kuzmin, G. a. Shafeev, V. V. Bukin, S. V. Garnov, C. Farcau, R. Carles, B. Warot-Fontrose, V. Guieu, G. Viau, *J. Phys. Chem. C* 114, 15266 (2010)
- [37] J. Piprek, *Semiconductor Optoelectronic devices: Introduction to Physics and Simulation*. (Elsevier Science, California, 2003), pp. 146
- [38] G. Z. Cao, *Nanostructures&Nanomaterials: Synthesis, Properties&Applications*. (Imperial College Press, London, 2004), p. 51