Journal of Computer & Robotics 9 (2), 2016 43-50

Optimization of Non-volatile Memory Cell and Energy Consumption in Robot Systems by Synthesized Silicon Nanoparticles via Electrical Discharge

Mehdi Mardanian

Department of Physics, Qazvin Branch, Islamic Azad University, Qazvin, Iran

Received 29 April 2016; accepted 26 July 2016

Abstract

In this paper, we propose to optimize manufacturing methods of memory cells by produced silicon nanoparticles via electrical spark discharge of silicon electrodes in water to reduce the energy consumption for low power applications. The pulsed spark discharge with the peak current of 60 A and a duration of a single discharge pulse of 60 μs was used in our experiment. The structure, morphology, and average size of the resulting nanoparticles were characterized by means of X-Ray Diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM). TEM images illustrated nearly spherical and isolated Si nanoparticles with diameters in the 3-8 nm range. The optical absorption spectrum of the nanoparticles was measured in the violet-visible (UV-V is) spectral region. By measuring of the band gap we could estimate the average size of the prepared particles. The silicon nanoparticles synthesized exhibited a photoluminescence (PL) band in the violet- blue region with a double peak at around 417 and 439 nm. It can be attributed to oxide-related defects on the surface of silicon nanoparticles, which can act as the radiative centers for the electron-holepairsre combination.

Keywords: silicon nanoparticles, synthesis, spark discharge, liquid.

---

1. Introduction

The size-dependent luminescent and nonlinear optical properties of semiconductor nano structure make them attractive candidates for a variety of technological applications. These materials constitute unique systems combining collective properties of solids with structural diversity of molecules which show distinctive photo-electrochemical properties. Among them silicon nanoparticles (Si-NPs) have attracted significant attention for many years due to the discovery of their various quantum phenomena and their possible integration with traditional Si transistors. Si-NPsare candidate in lasers, charge trapping, storage elements for future high density, low-voltage non volatile memory devices, data storage, energy source and sensor devices. The devices are based on surface modified wide band gap semiconductors and photo-electrochemical photocurrent switching effect. This effect has created a new platform for novel chemical switches, logic gates and other information processing devices.

---

* Corresponding author. Email: ma_mardanian@yahoo.com

Further, their promising applications in the fields of energy and electronic engineering are discussed.

It is well known that semiconductors with indirect band gap are not convenient for light emitting devices due to their intrinsic feature of weak interactions with photons. Among them is silicon. However, remarkable luminescence from silicon can be observed when the grain size decreases to the nano scale at which quantum confinement effect begins to be dominant, for example, the visible emissions from porous silicon, which has attracted extensively attention in the last decade, and Si-NPs [2]. Si-NPs present a growing interest due to their particular size-dependent optical properties leading to important photonic applications[3-7].To date, various methods have been developed for Si nanoparticles synthesis, including electrochemical etching [6], chemical vapor deposition [7] and pulse laser ablation [8-13]. Here, we developed a facile and novel procedure to synthesis Si-NPs by electrical discharge method in liquid environment which is an interesting technique because of simplicity of experimental setup, no need for vacuum equipments, low impurity introduction, less production steps leading to a cost-effective procedure to fabricate a high yield of nanoparticles [14-17]. In the present work, we prepared nearly spherical Si-NPs by spark discharge between bulk silicon electrodes in water. We studied microstructure, size distribution, and band gap energy of the Si-NPs produced.

There are some articles indicating Si-NPs can be synthesized by laser ablation of silicon wafer immersed in different liquid environment such as water, ethanol, and/or aqueous solution of sodium dodecyl sulfate [8-13]. Nevertheless there are a few published reports on synthesis of Si-NPs by electrical discharge method in liquid media. Before, the preparation of Si nanostructures including nano wires and nanoparticles by an arc discharge method in water has been performed by Liu et al. [18]. Kobayashi et al. could also fabricate Si-NPs through arc discharge in liquid nitrogen [19]. After etching, they obtained Si-NPs of 3-6 nm in diameter. Recently, Vonset al. have produced Si-NPs by spark discharge in gas media [20]. In this work we produced Si-NPs based on electrical spark discharge of Si electrodes immersed in water.

2. Experimental Details

The experimental setup for nano powder synthesis is schematically shown in Fig. 1. It consists of three main parts: a power supply system, chilling loop, and a reactor cell (glass beaker) with an anode and cathode inside. A spark discharge was ignited in 150 ml of water between two electrodes being immersed to a depth of 3 cm. The silicon plates were employed as electrodes. The optimal distance between the electrodes was kept constant at approximately of 1 mm to maintain a stable discharge. The alternating current (ac) spark discharge was initiated by applying a high frequency voltage of 8.5 kV.

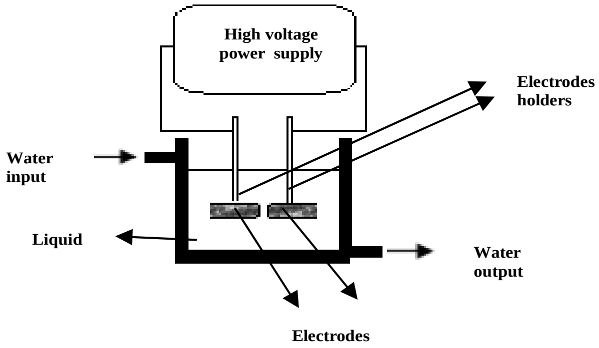

Fig. 1. Schematic diagram of the setup for nano powder synthesis by spark discharge in liquid

During the spark discharge, a bluish light radiation and bubbles containing the evaporated material of electrodes and products of water dissociation were observed between the electrodes. Small particles were formed though the mechanism of the condensation of Si vapor coming out of the melting surface of electrodes in result of cooling process in the surrounding water. With an extension of discharge time to 10 min, the solution became turbid. Most of the synthesized products were obtained as suspended powder. UV-Visible spectroscopy of the samples was taken by a Carry 500 spectrophotometer in the spectral region from 250 to 900 nm. Analysis of the crystalline structures was performed by XRD diffractometer (D8-Advance, Germany) with Cu-Kα radiation in 2θ range from 10° to 100°. The samples for TEM were prepared by dropping of the solution onto a copper grid coated with an amorphous carbon film and leaving them to dry in air. FTIR spectroscopy was conducted to investigate the surface properties of Si-NPs synthesized.

3. Results and Discussion

Fig. 2 shows the typical XRD pattern of the synthesized samples in water. It should be noted that the XRD was performed for the formed powder after drying of the colloidal solution for the not size-separated and possibly aggregated (agglomerated) particles just aiming to determine the phase composition of the synthesized powders.

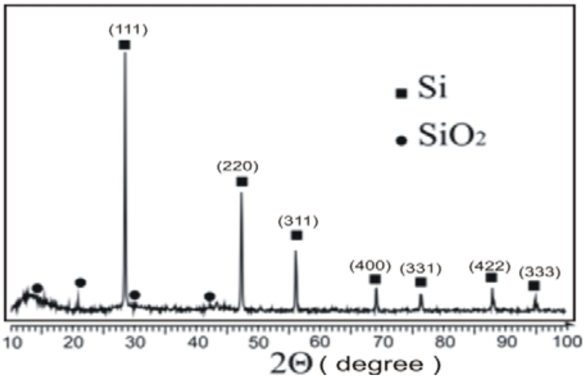

Fig. 2. Typical XRD pattern of the silicon nano powder prepared by spark discharge in water.

Therefore the XRD peaks of Si in Fig. 2 are rather sharp. The main diffraction peaks could be ascribed to (111), (220), (311), (400), (331), (422), and (333) of the lattice plane of cubic structured silicon. No amorphous silicon pattern is observed in XRD. The small peaks hardly distinguishable around 14°, 21°, 30°, and 42° are described to the SiO2 phase which can be generated during the spark discharge. FTIR spectroscopy confirms the possible formation of the oxide phase on the surface of particles. In Fig. 3 the vibration modes located at wave numbers 1064, 794, and 464 cm-1 are attributed to Si-O vibration bonds which could be evidence for the presence of oxide layer on the surface of synthesized particles.

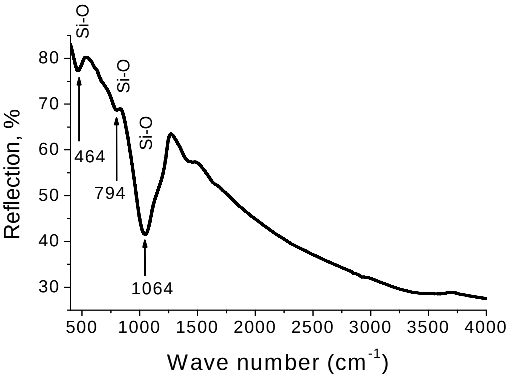

Fig. 3. FTIR spectra for Si-NPs synthesized by spark discharge in water

The results of UV-visible absorption measurement of suspended nanoparticles obtained in solution are shown in Fig.4. The spectrum appears to have a gradual increase in the absorption with decreasing the wavelength exhibiting two shoulders at about 370 nm (3.3 eV) and 290 nm (4.2 eV)related to the direct-gap absorptions and the absorption tail in the visible region associated with indirect transitions. It should be noted that bulk silicon is characterized by indirect band-gap absorption from 1.1 eV to 3.4 eV and two direct-gap transitions starting around 3.2eV (380 nm) and 4.2 eV (295 nm)[21]. The nano sized silicon particles indicate a blue-shifted absorption edge in comparison to the bulk Si. For the indirect transitions the absorption data in the region of the band edge can be described by the following relation:

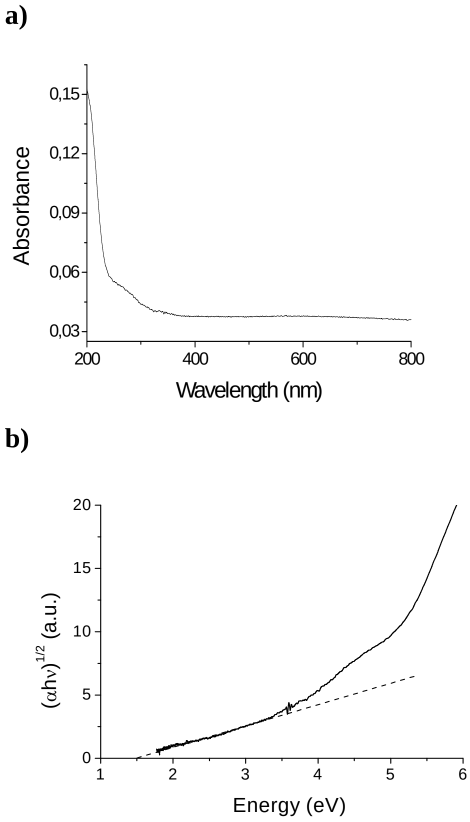

Fig. 4. UV-V is absorption spectrum of the Si-NPs produced by spark discharge between silicon electrodes in water (a) and absorption plotted as $(\alpha h\nu)^{1/2}$vs.hν (b). Dash line is extrapolation for determination of the band gap energy.

$$\alpha h\nu \propto (h\nu - E_g)^2 \qquad (1)$$

This equation can be used for the calculation of the band- gap energy (E_g) of the Si-NPs [10, 11]. For this purpose the absorption data should be re-plotted as $(\alpha h\nu)^{1/2}$ versus the photon energy hν, where α is the absorption coefficient measured. In such a plot, a linear behavior is expected in the region of indirect transitions. As can be seen from Fig. 4 (b) for Si-NPs synthesized, good agreement between the experimental data and a linear fit is observed for the energy interval from 2.2 to 3.3eV. A difference at lower energies could be due to the fact that absorption signal is generated through more than one mechanism. It is clear that different factors can affect the absorption process in Si-NPs, such as the size distribution function of nanoparticles, the surface states effect, and oxide layer defects and localized surface states can play an important role in lower energy region. The indirect band-gap energy for Si-NPs produced was estimated from the intercept of the straight line with the *x* axis to be about 1.5 eV. The result corresponds to a shift of $\Delta E=E_g-E_0=0.38$ eV from the band gap of the bulk Si ($E_0=1.12$ eV).

Delarue et al. [22] suggested the following empirical correlation between a size and electronic band gap of Si-NPs based on photoluminescence results and simulations using a linear combination of atomic orbitals (LCAO):

$$E_g = E_0 + \left(\frac{a}{d^b}\right) \qquad (2)$$

Where parameters *a* and *b* depend on the nature of the surface as well as a size and symmetry of NPs, and *d* corresponds to NP size. For relatively small (<10 nm) spherical Si-NPs these two parameters were calculated to be 3.73 and 1.39 for *a* and *b*, respectively. Using the relation (2) and the band-gap energy obtained from Fig. 4(b), the shift of ΔE=0.38 eV should correspond to a diameter of particles of 5 nm.

Fig. 5 (a) shows the representative TEM image of Si-NPs synthesized by spark electrical discharge in water. TEM observations indicate that Si-NPs generated in water are nearly spherical, isolated (without agglomeration) and similar in morphology. Nearly all particles have a size in the range of 3-8 nm. The maximum of this distribution is around 6 nm and the mean size of the particles is about 5±0.2 nm. The size value obtained for Si-NPs by using relation (2), is in close agreement with the TEM results. The accuracy of the calculated NP size from the relation (2) can be influenced by size distribution of particles, because the used values of the parameters *a* and *b* are valid for a size of NPs with less than 10 nm and can be not available for bigger ones.

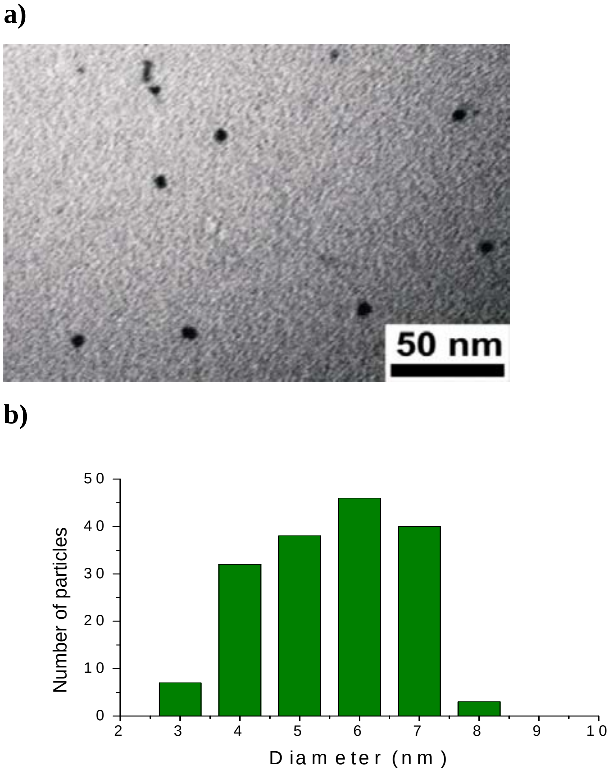

Fig. 5. TEM image (a) and size distribution (b) of the Si-NPs produced via spark discharge in.

It is well known that Bulk Si has no photoluminescence because of its narrow and indirect band gap. Nevertheless, impurities or defects can be introduced into Si to act as radiative centers. As the diameter of Si particles shrinks to several nano meters, it is possible that the nanoparticles become efficient light emitters resulting from the quantum confinement effect. The photoluminescence of Si nanostructures can be explained by the radiative recombination of electron-hole generated pairs in a confined quantum system. The main argument in favor of this interpretation, that has been adopted by many investigators, is that similar size effects were observed in Si nanostructures irrespective of the kind of surface passivation (hydrogen or oxygen passivation) [23]. Recently, it has been also reported that the surface states and defects can play a significant role in luminescence process of silicon nano crystals [24-26]. But the origin of the PL is still a subject of debate. The PL spectra of the synthesized Si-NPs at room temperature are shown in Fig. 6.

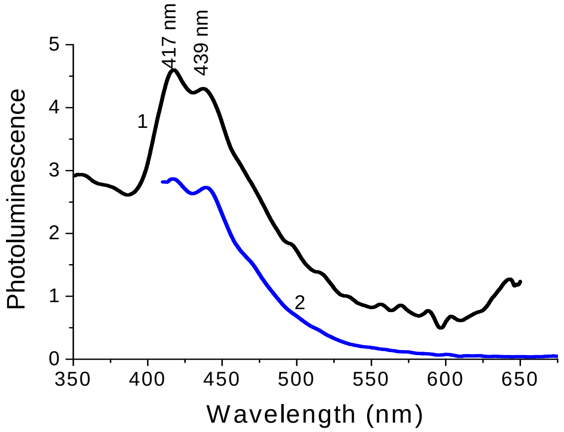

Fig. 6. The PL spectra for the Si-NPs synthesized via spark discharge in water. Excitation wavelengths: 270 nm (curve 1) and 365 nm (curve 2).

The PL exhibits a prominent emission band in the violet-blue range with a double peak around 417 and 439 nm for both applied excitation wavelengths.

It should be pointed out that the excitation wavelength of 365 nm (3.4 eV) is located near the direct band gap of the Si-Nps. Nevertheless the observed violet-blue light emission in the PL spectrum of our samples cannot be simply attributed to the quantum confinement effect of the Si-NPs with diameters in the 3-8 nm range. Because the bulk excitonic radius for Si is about 4 nm and the emission through the direct electron-hole recombination across the Γ-Γ direct band gap should be observed for nano crystals with smaller than this size [21]. Note that only few particles in this size range were detected in the TEM images of our sample. Besides, we have not observed any remarkable shift of the emission peak position when the excitation wavelength moves from 270 to 365 nm.

Therefore radiative recombination via the defect centers formed in the surface oxide layer of the Si-

NPs or at the interface between the Si nano crystal and Si oxide layer is the most possible mechanism of the observed blue PL of our Si nano crystals. Indeed, according to the FTIR spectra, our Si-NPs are covered with oxygen (oxide). Some oxide-related defects might be formed within the surface oxide layer of the Si-NPs which might act as the radiative centers for the electron-hole recombination [24-25]. The existence of the dangling bonds on the surface results in various surface states deep in the energy gap. As the electron-hole pairs are generated, most likely through the photo excitation in the crystalline Si cores, light emission is observed after recombination of electrons and holes at the luminescent centers located at the core - oxide layer interface or in the oxide surface [26]. Previously the very similar violet-blue PL spectra of Si-Nps were reported by Takashi Uchino et al [27] and Shikan Yang et al. based on the proposed structural model Uchino also explained the origin of blue PL from the nano meter-sized silica particles by a radiative recombination via the defect centers formed in Si oxide. But the PL spectrum reported for Si-NPs of the 4.5 nm diameter that was generated through laser ablation in water by Shikan Yang et al. the authors attributed to intrinsic nano crystal states rather than to surface/defect recombination. Therefore the further detailed excitation spectral studies for the PL origination are required.

4. Conclusion

There is no doubt that the attention paid to the field of Si NPs will increase more creative research results are expected to be presented and this material will have an immeasurable influence on the future society. In according to the results and discussion presented above, Si-NPs have been synthesized by a simple, inexpensive and effective technique of electrical spark discharge between bulk silicon electrodes in water. This method allowed us to produce Si-NPs with the average diameter of 5 nm. Indeed electrical discharge in solution is a nano meter-scale engineering technique with a possibility to scale-up the process. The synthesis rate of Si nanoparticles in our experiments by using the present apparatus varied in range of 10 – 40 mg/ h depending on peak current and pulse duration of discharge. The synthesis rate increased with increasing of discharge current and decreasing of pulse duration. Si-NPs are formed through the mechanism of the primary nucleation of the evaporated atoms from the electrodes in the plasma plume and a growth of the embryonic particles. The synthesized semiconductor nanoparticles can be used in wide generation of memory devices and energy sources with higher densities, higher speeds, lower power, more functionality and lower costs. We hope and are confident around high ability aiming to go beyond those limitations and potentially replace all or most of the existing memory manufacturing technologies by obtained semiconductor nanoparticles via above mentioned method. Despite available limitations, the field of conventional memories would continue to flourish and memory device scientists will find the way to meet these challenges and may even develop a ‘unified memory’ with low cost, high performance, and high reliability for future electronic systems. Progress towards a viable new resistive memory technology relies on fully understanding the mechanisms responsible for switching and charge transport, the failure mechanisms, and the factors associated with materials reliability.

References

[1] J. H. Park, L. Gu, G. Maltzahn, E. Ruoslahti, S. N. Bhatia and M. J. Sailor, "Magnetic luminescent porous silicon microparticles for localized delivery of molecular drug payloads" Journal Nature Mater, vol. 8, pp. 331-338, 2009.

[2] L. Russo, F.Colangelo, R.Cioffi, I. Rea and L. De Stefano, "A mechanochemical approach to porous silicon

nanoparticles fabrication" Journal of Materials, vol. 4, pp. 1023-1033, 2011.

[3] R. J. Walters, G. I. Bourianoff and H. A. Atwater, "Photoluminescence quantum efficiency of dense silicon nanocrystals ensembles in SiO2" Journal of Physical Review, vol. 4, pp. 3021-3024, 2006.

[4] M. Stupca, M. Alsalhi, T. Al Saud, A. Almuhanna and M. H. Nayfeh, "Enhancement of polycrystalline silicon solar cells using ultrathin films of silicon nanoparticle" Journal of Applied Physics Letters, vol. 91, pp. 063107-063112, 2007.

[5] V. Chirvony, A. Chirvonaya, J. Ovejero, E. Matveeva, B. Goler, D. Kovalev, A. Huygens and P. de Witter, "Surfactant-modified hydrophilic nanostructured porous silicon for the photosensitized formation of singlet oxygen in water" Advanced Matterials, vol. 19, pp. 2967-2972, 2007.

[6] V. Svrcek, D. Mariotti, T. Nagai, Y. Shibata, I. Turkevych and M. Kondo, " Photovoltaic applications of silicon nanocrystal based nanostructures induced by nanosecond laser fragmentation in liquid media" Journal of Physical Chemistry C, vol. 115, pp. 5084-5093, 2011.

[7] F. Priolo, G. Franzo, D. Pacifici and V. Vinciguerra," Role of energy transfer on the optical properties of undoped and Er-doped interacting silicon nanocrystals" Journal of Applied Physics, vol. 89, pp. 264-273, 2001.

[8] C. Grigoriu, Y. Kuroki, I. Nicolae, X. Zhu, M. Hirai, H. Suematsu, M. Takata and K. Yatsui, "Photo and cathodoluminescence of Si/SiO2 nanoparticles produced by laser ablation" Journal of Optoelectronics and Advanced Matterials, vol. 7, pp. 2979-2984, 2005.

[9] K. Watanabe, K. Sawada, M. Koshiba, M. Fuji and S. Hayashi, "Photoluminescence decay-dynamics of nanoparticles prepared by pulsed laser ablation" Applied Surface Sciences, vol. 635, pp. 197-198, 2002.

[10] N. G. Semaltianos, S. Logothetidis, w. Perrie, S. Romani, R. J. Potter and S. P. Edwardson, "Silicon nanoparticles generated by femtosecond laser ablation in a liquid environment" Journal of Nanoparticles Research vol. 3, pp. 9623-9625, 2009.

[11] Sh. Yang, W. Cai, H. Zeng and Zh. Li, "Polycrystalline Si nanoparticles and their strong aging enhancement of blue photoluminescence" Journal of Applied Physics, vol. 104, pp. 23516-23519, 2008.

[12] Sh. Yang, W. Cai, H. Zhang, X. Xu and H. Zeng, "Size and structure control of Si nanoparticles by laser ablation in different liquid media and further centrifugation classification" Journal of Physical Chemistry C, vol. 113, pp. 19091-19094, 2009.

[13] R. Intartaglia, K. Bagga, F. Brandi, G. Das, A. Genovese, E. Di Fabrizio and A. Diaspro, "Luminescent silicon nanoparticles prepared by ultrashort pulsed ablation in liquid for imaging applications" Journal of Physical Chemistry C, vol. 115, pp. 510-518, 2012.

[14] W.G. Graham and K.R. Stalder, "Plasmas in liquids and some of their applications in nanoscience" Journal of Applied Physics, vol. 44, pp. 174037-174042, 2011.

[15] N. Parkansky, B. Alterkop, R.L.Boxman, S. Goldsmith, Z. Barkay and Y Lereah, "Pulsed discharge production of nano and microparticlein ethanol and their characterization" Powder Technology, vol. 150, pp. 36-41, 2005.

[16] V.S. Burakov, N.A. Savastenko, N.V. Tarasenko and E.A. Nevar, "Synthesis of nanoparticles using a pulsed electrical discharge in a liquid" Journal Applied Spectroscopy, vol. 75, pp. 114-124, 2008.

[17] V. S. Burakov, E. A. Nevar , M. I. Nedel'ko, N. A. Savastenko and N. V. Tarasenko, "Spectroscopic diagnostics for an electrical discharge plasma in a liquid" Journal Applied Spectroscopy, vol. 76, pp. 856-863, 2009.

[18] S. Liu, M. Kobayashi, S. Seiichi and K. Kimura, "Synthesis of silicon nanowires and nanoparticles by arc discharge in water" Journal of Chemical Communication, vol. 35, pp. 4690-4692, 2007.

[19] M. Kobayashi, S. Man Liu, S. Sato, H. Yao and K. Kimura, "Optical evaluation of silicon nanoparticles prepared by arc discharge method in liquid nitrogen" Journal of Applied Physics, vol. 8A, pp. 6146-6152, 2006.

[20] V.A. Vons,L. C. P. M. de Smet, D. Munao, A. Evirgen, E.M. Kelder and A. Schmidt-Ott, "Silicon nanoparticles produced by spark discharge" Journal of Nanoparticles Research, vol. 13, pp. 4867-4879, 2011.

[21] J. P. Wilcoxon, G. A. Samara and P. N. Provencio, "Optical and electronic properties of Si nanoclusters synthesized in inverse micelles" Journal of Physical Review B, vol. 4, pp. 2704-2714, 1999.

[22] C. Delerue, G. Allan and M. Lannoo, "Theoretical aspects of the luminescence of porous silicon" Journal of Physical Review B, vol. 48, pp. 11024-11028, 1993.

[23] M. Wolkin, J. Jorne, Pm. Fauchet, G. Allan and C. Dederue, "Electronic states and luminescence in porous silicon quantum dots: the role of oxygen" Journal of Physical Review Letters, vol. 82, pp. 197-200, 1999.

[24] S. W. Lin and D. H. Chen, "Synthesis of water-soluble blue photoluminescence silicon nanocrystals with oxide surface passivation" Journal of Small, vol. 5, pp. 72-76, 2009.

[25] X. Y. Chen, Y. F. Lu, Y. H. Wu, B. J. Cho, M. H. Liu, D. Y. Dai and W. D. Song," Mechanism of photoluminescence from silicon nanocrystals formed by pulsed laser deposition in argon and oxygen ambient" Journal of Applied Physics, vol. 93, pp. 6311-6319, 2009.

[26] S. Yang, W. Li, B. Cao, H. Zeng and W. Cai, "Microstructure and dry-sliding wear properties of TiC-reinforced composite coating prepared by plasma-transferred arc weld-surfacing process" Journal of Physical Chemistry C, vol. 43, pp. 21056-21062, 2011.

[27] T. Uchino, N. Kurumoto and N. Sagawa, "Silicon nanoparticles produced by spark discharge in liquid" Journal of Physical Review B, vol. 73, pp. 3203-3207, 2006.