

## Nanocrystalline silicon and carbon nanotube nanocomposites prepared by pulsed laser fragmentation\*

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**Abstract:** This paper outlines the synthesis of nanocrystalline silicon (nc-Si) by nanosecond pulsed laser fragmentation of Si micrograins in liquid solutions, and characterization of the products. We compare micrograin fragmentations in deionized water, and in undoped and phosphorus-doped ethylpolysilicate ( $\text{C}_2\text{H}_5\text{O}[\text{SiO}(\text{C}_2\text{H}_5\text{O})_2]_n \text{C}_2\text{H}_5$ ) based polymers. We show that dissolution and subsequent laser fragmentation of micrograins is more efficient in both polymeric media than in water. In the case of water, micrograin surface wetting by ethanol prior to introduction into water is essential to achieve fragmentation. Prepared nc-Si/polymer nanocomposites display visible photoluminescence (PL) ( $\sim 430$  nm) at room temperature. The phosphorus polymer induces a blue shift of the PL peak. In addition, induced shock waves generated at sufficiently high laser irradiation intensities ( $>4.3$  mJ/pulse) cause carbon nanotube (CNT) cavities to be filled by freshly prepared luminescent nc-Si/polymer nanocomposite.

**Keywords:** silicon nanocrystals; photoluminescence; laser ablation; carbon nanotubes.

### INTRODUCTION

The possibility of encapsulating nanocrystalline molecules inside the cavity of carbon nanotubes (CNTs) is opening up new routes to engineer and tune the electronic properties of such new nanocomposite materials [1]. On the other hand, an observation of visible photoluminescence (PL) in nanocrystalline silicon (nc-Si) [2] was greeted with great interest [3,4]. Control of optical response by modifying the size or surface chemistry of Si nanocrystals has become one of the most challenging aspects of recent semiconductor research [5]. However, the high surface tension of molten Si makes direct filling of a CNT cavity impossible [6]. This challenge can be overcome by using nc-Si dispersed in solutions, which offers the potential to achieve encapsulation in this cavity. Simple immersion of CNTs in organic solutions containing nc-Si results in surface threshold values that allow nanotube wetting and introduction of luminescent nc-Si into the cavity [7,8].

During the last decade, pulsed laser ablation in liquid media has attracted much attention in fabrication of colloidal nanoparticles and modifications to surface chemistry [9]. Pulsed laser ablation in liquid is a cold-wall, and the extreme nonequilibrium conditions are advantageous for the synthesis of

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materials that prefer high-pressure and -temperature ambience [9,10]. When Si micrograins in a colloidal suspension are irradiated by nanosecond laser pulses, the grains can be transiently heated to temperatures much higher than the surrounding and less-absorbing liquid. A solution containing such local hot spots exhibits novel dynamic properties, allowing fragmentation of grains and nc-Si formation [11]. The nc-Si that is fabricated by nanosecond pulsed fragmentation in solution has unique surface chemistry and a large range of variations that can be applied in the elaboration of materials. Recently, luminescent nc-Si having a quantum confinement effect with pulsed laser fragmentation has been prepared [11]. Direct formation of nc-Si in organic-based polymers avoids nanocrystal pollution, improves its surface passivation, and enhances its PL properties [11]. Transparent ethylpolysilicate polymers are now commercially available and well established in current Si technologies (electronics, photovoltaics) [12]. Such polymers can passivate the Si surface and in the presence of dopants (boron, phosphorus) are used for shallow doping of the Si wafers in the fabrication solar cell emitters [13].

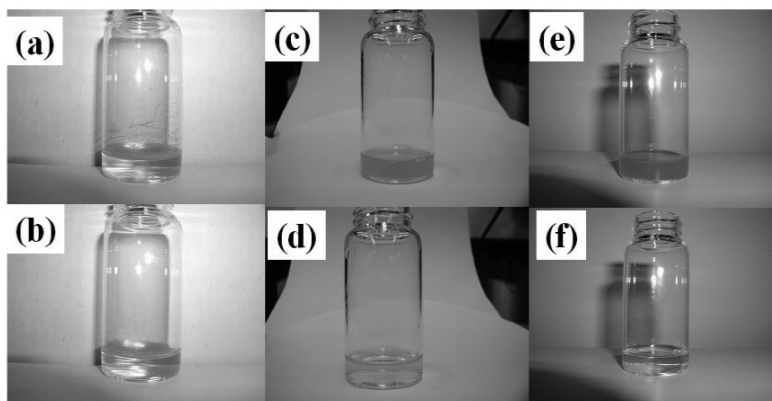
In this article, we explore the possibility for direct nc-Si formation in undoped and phosphorus-doped ethylpolysilicate polymer by pulsed nanosecond laser fragmentation. We demonstrate that fragmentation of Si micrograins dispersed in liquid polymers allows room-temperature preparation of luminescent nc-Si/polymer composites. A blue shift of the PL peak can be achieved by varying the phosphorous concentration in the polymer host matrix. Moreover, shock waves induced by fragmentation allow CNT cavities to be filled with luminescent nc-Si/polymer nanocomposites.

## EXPERIMENTAL

Micrograins of nc-Si were prepared by electrochemical etching. The technique involves the etching of a Si wafer (p-type boron-doped, <100>, 0.1 ohm-cm, thickness 0.525 mm) for 2 h at 1.6 mA/cm<sup>2</sup> constant current in HF:ethanol electrolyte (1:4) and then subsequently mechanically pulverized [12]. The fine nc-Si was harvested by repeated sedimentations in ethanol. After ethanol evaporation in an oven at 323 K, the fine nc-Si powder was dispersed to prepare colloidal solutions of 0.1 wt %. In this study, commercially available undoped and phosphorus-doped (Si-59000, P-59250 Tokyo Ohka Kogyo Co., Ltd.) polymers have been used. The doped and undoped polymer, ethylpolysilicate ( $\text{C}_2\text{H}_5\text{O}[\text{SiO}(\text{C}_2\text{H}_5\text{O})_2]_n\text{C}_2\text{H}_5$ ) is dissolved in ethanol and ethyl acetate. The colloidal solutions, nc-Si micrograins/polymer and solvent were sonicated for 10 min and solidified in an air atmosphere at 323 K for 24 h.

Micrograins precipitated at the bottom of the container and were then collected and dried in an oven at 323 K. Subsequently, the precipitated micrograins were dispersed in 5 ml of deionized water or in the polymer solutions. For the laser fragmentation, 0.01 wt % Si micrograin colloidal solutions (liquid undoped polymer, phosphorus-doped polymer, water) were prepared. The colloidal solutions were sonicated for 10 min. In order to obtain homogenous dispersion of the grains in deionized water, the surface of Si micrograins was wetted by ethanol (20 drops). Wetting by ethanol prevented the hydrophobic Si micrograins from accumulating at the water-atmosphere interface. Figure 1a shows the accumulation of micrograins when ethanol was not applied. Fragmentation was achieved by irradiating the solution with a pulsed laser (Nd:YAG, 355 nm, 30 Hz, 8 ns) at 5.9 mJ/pulse fluence for 2 h and at room temperature. The laser beam was focused into a 1-mm diameter spot on the liquid surface by a lens with a focal length of 250 mm. During the irradiation, the glass container was closed and rotated. After irradiation, the colloidal suspension in polymers were again sonicated for 10 min and then dried for solidification in air at 323 K for 24 h. This produced self-supporting polymer samples (25 mm<sup>2</sup>) with dispersed nc-Si for PL measurements.

In order to introduce nc-Si in CNTs, Si micrograins (0.01 wt %) were homogeneously dispersed in 30 ml solution of undoped polymer and CNTs (0.01 mg). Then, 5 ml of such solution (micrograins/CNTs/polymer) was poured into a glass container, and irradiated by a pulsed laser (Nd:YAG, 355 nm, 30 Hz, 8 ns) at a laser fluence ranging from 0 to 6 mJ/pulse for 2 h at room temperature. The laser beam was focused on the liquid surface, and the glass container was rotated during irradiation.



**Fig. 1** Photos of 0.01 % Si micrograins in 5 ml deionized water (a) before and (b) after laser irradiation for 2 h at a fluence of 5.9 mJ/pulse. (c) Figure of 0.01 % ethanol wetted Si micrograins in 5 ml deionized water and undoped polymer solution (e). (d) and (f) display solutions after laser irradiations (2 h at a fluence of 5.9 mJ/pulse), respectively.

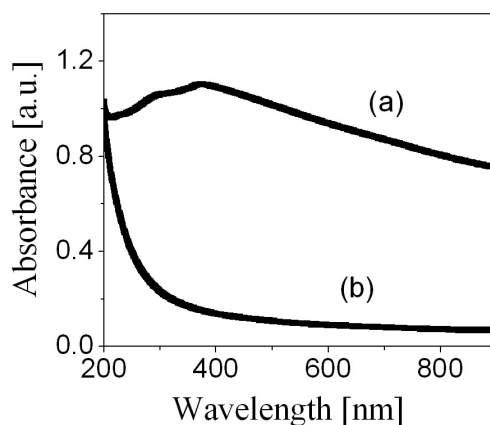
After solidification (air atmosphere, 24 h) hard block compounds of nc-Si/polymer and nc-Si/polymer/CNTs were mechanically crushed and dispersed in deionized water. A droplet of the aqueous solution was deposited onto a copper grid to enable transmission electron microscopy (TEM) and scanning electron microscopy (SEM) observations. SEM images were captured with a Hitachi S-4800 microscope with 30 kV acceleration voltage and 1 nm point-to-point resolution. Energy dispersive X-ray spectroscopy (EDS) was employed to determine local elemental concentrations. The high-resolution transmission electron microscopy (HR-TEM) observations were performed with a microscope with 200 kV acceleration voltage (JEOL, JEM-2010). Electron diffraction was employed to perform more localized crystalline structure analysis of the Si nanoparticles. The PL of solid self-supporting layers was measured at 300 K with an excitation of a He-Cd cw laser at 325 nm. The emission spectra were recorded by a spectrometer (JASCO, CT-10) using a photomultiplier as a detector.

## RESULTS AND DISCUSSION

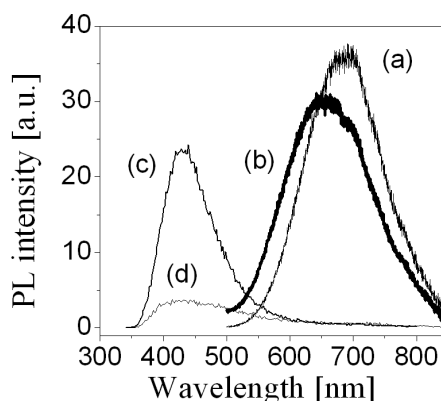
Figure 1a displays a photo of 0.01 % Si grains in 5 ml deionized water. Hydrophobic Si micrograins stayed on the water surface. Even after laser irradiation (2 h at a fluence of 5.9 mJ/pulse), no visible change is observed and the micrograins were still observed at the surface (Fig. 1b). This problem is overcome by micrograin surface wetting with a small amount of organic solvent (i.e., ethanol). The result is shown in Fig. 1c whereby the micrograins are homogeneously dispersed in the solution. Figure 1d shows the same solution of Fig. 1c after micrograin fragmentation due to irradiation by pulsed laser. Intentional wetting of micrograin surface was not necessary for the polymer-containing solutions, as ethanol was already present and the homogeneous dispersion was naturally achieved. After dispersion, the colloid exhibits a yellow coloration (Fig. 1e). It is observed that at lower laser fluence (<1.13 mJ/pulse) in water and undoped/phosphorus-doped polymers, the solution color changed to dark brown, and prolonged laser irradiation did not induce any additional color change, therefore remaining dark brown. At higher laser fluence and prolonged laser irradiation, the solution became transparent. Figure 1f shows the undoped polymer solution after laser irradiation for 2 h at fluence of 5.9 mJ/pulse. However, it can be observed that (Fig. 1d) the color of the water solution is slightly yellow under the same laser irradiation conditions.

A few concomitant processes are responsible for the fragmentation Si micrograins. After the absorption of the laser pulses, micrograin fragmentation can be induced by either a photothermal process,

in which the particles vaporize at boiling temperature or through Coulomb explosion induced [14] by electron ejection from either a thermionic [15] or multiphoton ionization process [16]. The strong electric field generated by the laser causes the electron avalanche near the Si grain and the breakdown of the liquid. In our experiments, a bright spot was clearly observed near the surface, and explosion sounds due to the optical breakdown of the liquid (water/polymers) were also audible. These explosions are caused by collapsing vaporized cavitations bubbles, and by the fragmentation of micrograins that accidentally diffuse under the beam. A consequence of all the above processes is the formation of shock waves that are then accelerated at large distances with still sufficient energy to fragment particles weakly attached to micrograins [17]. The description of the processes above is likely to apply just for Si micrograins that are homogeneously distributed in the liquid. Therefore, ethanol wetting is an essential step to promote fragmentation and the unsuccessful fragmentation of the micrograins in Fig. 1b is consequently justified. It is also observed that the fragmentation is more efficient in the case of both polymers. It is believed that the organic nature of the polymers improves micrograin surface wetting and micrograin solubility. In addition, the higher polymer viscosity and the higher polymer density contribute to enhance the propagation of the shock waves, providing more efficient fragmentation. Figure 2 shows the absorbance of ethanol-wetted micrograins in deionized water. Curve a represents the absorption of the solution before irradiation, and curve b is the absorbance of the same solution after the fragmentation process at 5.9 mJ/pulse fluence. It is observed that the micrograins have a significant absorption cross-section at 355 nm wavelength, which is the wavelength of the laser used for the fragmentation. Therefore, efficient fragmentation of the Si micrograins could be achieved under irradiation. Curve b shows that the absorbance is drastically decreased after fragmentation. TEM and SEM images clearly show that Si micrograins in water are fragmented into Si particles with diameter less than 60 nm. On the other hand, fragmentation in polymer has produced particles with smaller diameters and within the limit of quantum confinement (<10 nm) [11]. One important advantage of introducing nc-Si into SiO<sub>2</sub>-based polymers is that the solidification improves the PL efficiency through the SiO<sub>2</sub> surface passivation [12]. In addition, the nanocrystal optical properties can be tuned by polymer doping [12]. Figure 3 shows PL properties of the nc-Si due to the presence of phosphorus in the polymer. Curve a in Fig. 3 represents the PL intensity as a function of wavelength for nc-Si prepared by electrochemical etching and embedded in undoped polymers after solidification. Curve b in Fig. 3 displays PL spectra of phosphorus-doped polymer. The presence of phosphorus induced an efficient modification of the surface terminations that is much more pronounced for small nanocrystals. As a result, a blue shift of the PL peak from 690 to 650 nm is observed. The nanosecond pulsed laser fragmentation induces a larger blue shift of the PL maxima. In Fig. 3, curve c denotes nc-Si embedded in undoped polymer and curve



**Fig. 2** Corresponding absorbance of aqueous colloidal solutions before (curve a) and after (curve b) nanosecond laser irradiation, respectively.

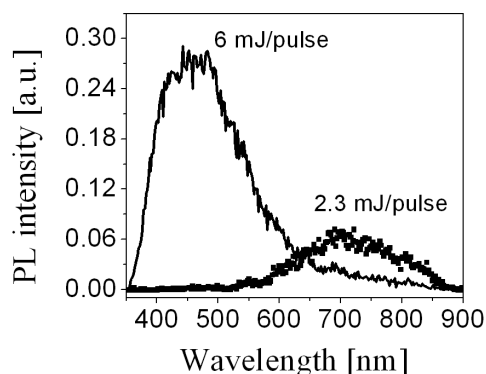


**Fig. 3** PL intensity as a function of wavelength for nc-Si in undoped polymer (curve a) and phosphorus-doped solid polymer (curve b) is shown. Curve c denotes that for nc-Si embedded in undoped solid polymer and curve d phosphorus-doped polymer after laser fragmentation at fluence 5.9 mJ/pulse for 2 h.

d corresponds to nc-Si in phosphorus-doped solid polymer after laser fragmentation (5.9 mJ/pulse, 2 h). It is assumed that the blue shift is due to the formation of smaller size particle and quantum confined nc-Si compared to samples prepared by electrochemical etching [11]. Significant blue shift of PL peak is noticed (curves c, d in Fig. 3) also due surface passivation of nc-Si by a layer of SiO<sub>2</sub>. Similar to the electrochemically etched nc-Si, slight blue shift of the PL peak (about 10 nm) is recorded when the solution contains phosphorus (curve d). We have also verified that laser irradiation and solidification of polymers is not sufficient to produce such luminescence properties [11].

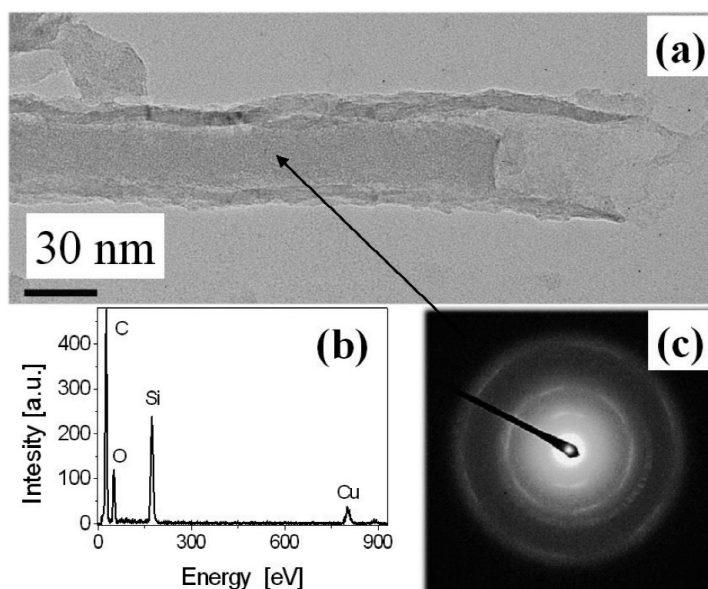
One can speculate whether or not the shock waves propagating through the solution could be useful for producing new types of nanocomposite. The prepared nc-Si with unique surface chemistry might exhibit to a decreased surface tension that could facilitate the insertion of nc-Si in narrow gaps such as within nanotubes cavities. We have then tried to use shock waves propagating through the polymer to stabilize freshly fragmented luminescent Si nanocrystals/polymer nanocomposite into CNT cavities. Similarly to the fragmentation of micrograins (Fig. 1f), one can observe that the suspension (micrograins/polymer/nanotubes) loses its light yellow color after irradiation with sufficiently high intensities (>4 mJ/pulse), and the solution becomes more transparent in the visible region. It is observed that due to the presence of CNTs, the fragmentation occurred at slightly higher irradiation intensities [11].

It could be argued that CNT exposure to laser irradiation might not be beneficial. Nevertheless, at low concentration, dispersed CNTs have been shown to have a weak absorption at 355 nm wavelength and most of the laser energy goes into the fragmentation of the micrograins [18]. Similarly to the results obtained for the fragmentation of micrograins (Fig. 3, curves c and d), an increased irradiation fluence leads to a blue shift of the PL peak. Figure 4 displays the PL spectra of solidified undoped polymer/micrograins/CNT solutions after the fragmentation at two different laser irradiation fluences. A very large blue shift (more than 300 nm) is observed as the solution is irradiated with a fluence of 6 mJ/pulse, compared to smaller shifts obtained at low fluence (2.3 mJ/pulse).



**Fig. 4** PL spectra of undoped polymer containing CNTs in solid phase after irradiation for 2 h at two different nanosecond pulsed laser irradiation fluences.

As the fragmentation occurs, the generated shock waves introduce freshly formed nc-Si embedded in polymer solution in the CNT cavities. It is observed that nanotube cavities are fully filled with nc-Si/polymer composite. When the fragmentation occurs ( $>4$  mJ/pulse), the solution loses its light yellow color and an increased content of Si in the CNTs cavity is observed. SEM and EDS analysis confirmed systematically excess of Si content when fragmentation occurred. Also, a detailed HR-TEM analysis has been performed to confirm the presence of Si nanocrystals within the CNT cavities. Figure 5a displays a typical image of a filled multiwall CNT with inner diameter of 50 nm after the solution was irradiated at laser fluence of 6 mJ/pulse. EDS analysis also confirm the presence of Si when fragmentation occurred (Fig. 5b). The corresponding electron diffraction pattern (Fig. 5c), in addition to EDS, revealed as well as Si diffraction rings that could be assigned to the lattice planes  $\langle 111 \rangle$ ,  $\langle 220 \rangle$ ,  $\langle 311 \rangle$  with cubic phase.



**Fig. 5** (a) HR-TEM image of nc-Si fragmented by a laser fluence of 6 mJ/pulse. Plot (b) displays local elemental analysis and image (c) corresponding selected area electron diffraction pattern in the tube (indicated by an arrow).

At low CNT concentrations within the polymer solution and low applied laser irradiation intensities, the micrograin fragmentation occurs. From the above discussion, one can assume that the shock wave is a major driving force to introduce freshly formed nc-Si/polymer composite into CNT cavities. The impact of these shocks can be important as they propagate through the liquid media [19]. In the medium with acoustic nonlinearity, which is our case, the higher amplitudes propagate at supersonic velocities, which makes the front of the pressure wave steeper [17]. Consequently induced reflux introduces the nc-Si together with hydrophilic polymer into the CNT cavities.

## CONCLUSIONS

Fragmentation of micrograins in water in undoped and phosphorus-doped polymers was investigated. We demonstrated an effective method for the fabrication of room-temperature PL Si nanocrystals (nc-Si) by nanosecond laser fragmentation of electrochemically etched Si micrograins. In the case of water, wetting of Si micrograin surface by ethanol prior to introduction into water is essential to achieve fragmentation. The phosphorus-doped polymer modifies the nc-Si surface states and induces a blue shift of PL peak. Ethylpolysilicate-based polymer naturally wets the surface, and also the fragmentation process is shown to be more efficient. Shock waves produced during the fragmentation process induce the insertion into CNT cavities of the freshly formed luminescent nanocrystals embedded in polymer.

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