Synthesis of silicon nanoparticles by laser ablation at low fluences in water and ethanol

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Abstract
Colloidal silicon nanoparticles (Si-nc) where synthesized by laser ablation of a solid Si target in water and ethanol. The target was immersed in a vessel containing the solvent and irradiated during 5 and 10 min at different fluences: 0.530, 0.608, 0.687 J cm⁻². Ablation was carried out using a laser wavelength of 1064 nm. The obtained colloidal nanoparticles were irradiated after the synthesis to evaluate if laser fragmentation could be produced. In addition, a series of nanoparticles using ethanol as liquid medium was synthesized ablating with 532 nm. Colloidal nanoparticles were structurally characterized by Raman spectroscopy and Transmission Electron Microscopy. Size of the Si-nc were calculated by the theoretical models: Bond Polarizability Model (BPM) and One- Phonon Confinement Model (PCM), where nanocrystals ranging from 2 to 11 nm were found.

Introduction
Silicon is one of the most important semiconductor materials for electronic devices due to its abundance on earth crust. Generally, silicon has been regarded as unsuitable for light emitting devices due to its indirect optical bandgap [1, 2]. Nevertheless, it is the most important material for semiconductor devices fabrication due to it has outstanding properties. Recently, applications for optoelectronic devices have been examined since efficient visible photoluminescence was observed in silicon nanoparticles [3], this is because of the differences in electronic properties they exhibit from bulk material due to their low-dimensional size, which results in quantum confinement of the electrons in the nanoparticles [4]. Silicon nanoparticles are zero dimensional, so their electronic structure may transform from indirect to direct band gap, which makes possible to have light emissions by an indirect gap semiconductor. Apart from optoelectronic devices, silicon nanoparticles have possible applications in the fields of cell biology and medicine [5].

Synthesis of silicon nanoparticles have been successfully achieved using chemical methods [4]; however, the problem with these methods is that they produce toxic or non-environmentally friendly residues from the precursors. Laser ablation of a solid target immersed in a liquid (LAL), is a good alternative to fabricate nanoparticles [6–10] without toxic residues generation [11]. The LAL method consists in ablating a bulk solid target immersed in liquid media.

Monodisperse colloids are difficult to produce by LAL without compromising colloidal purity, hence the LAL process is often accompanied by laser fragmentation in liquids (LFL) and laser melting in liquids (LML). LFL aims at downsizing particles from micro and nanometer sizes into smaller ones. While LML produces a size increase or reshape of dispersed particles due to coalescence of molten material ejected from the target [11, 12]. These techniques could allow precise size control of the synthesized nanoparticles.
To determine the size of the nanoparticles transmission electron microscopy (TEM) is the most common technique; nevertheless, this is an expensive and complicated method, as well as slow for measuring a large number of samples, due to that it involves special sample preparation and sophisticated equipment.

It has been reported that decreasing size of silicon crystals, induces shifts on their Raman spectra in comparison with the signal of bulk silicon \[6, 13, 14\].

To calculate the size of the Si nanoparticles from the experimental Raman spectra, two theoretical models that describe the size dependence on the shift of the phonon peak have been used. The Bond Polarizability Model (BPM) \[13\], that describes the polarizability of a nanocrystalline system calculated by the sum of the contributions of each bond for a particular size, and the modified One-Phonon Confinement Model (PCM) \[14\], that describes the Raman spectrum of a nanocrystal as a function of its crystal momentum, phonon frequency, phonon dispersion, and the degree of confinement. The degree of the phonon confinement influences the width and position of the principal Raman peak.

In this work, silicon nanoparticles were obtained by laser ablation of a bulk silicon target in water and ethanol and the average nanocrystal sizes were calculated from the theoretical models using the experimental data obtained from Raman spectroscopy measurements.

**Experimental**

Silicon nanoparticles were synthesized by laser ablation of solids in liquids at different fluences. For the synthesis, the 1064 nm emission of a Q-switched pulsed Nd:YAG laser, with pulse width of 6 ns, spot size of 9 mm, 10 Hz repetition rate and maximum output energy of 600 mJ per pulse was used. Thefluence was calculated by measuring the incident energy on the target. Spot size was kept constant and the output energy was modified by changing the delay time of the Q-switch in order to get fluence values of 0.687, 0.608 and 0.530 J cm\(^{-2}\). The liquid media were water and ethanol. Additionally, ablation at 532 nm using the second harmonic generator on a Si target immersed in ethanol was performed to obtain a series of samples and study the effect of photon energy on the size of the nanoparticles.

An n-type silicon pellet was immersed in a glass vessel with 5 ml of water or ethanol. The pellet was irradiated during 5 or 10 min using fluences of 0.687, 608 and 0.530 J cm\(^{-2}\) (figure 1(a))). Irradiation time was increased from 5 to 10 min in order to increase nanoparticles concentration in the liquid. The obtained colloidal nanoparticles from water and ethanol were post-treated with the laser at 1064 nm to induce fragmentation. These experiments were carried out using an optical lens with 10 cm of focal length, focusing the central part of the Si-nc suspension during 10 min using fluence values of 55, 49 and 43 J cm\(^{-2}\) for the samples synthesized at 0.687, 0.608 and 0.530 J cm\(^{-2}\), respectively (figure 1(b))).

The samples were structurally characterized by Raman spectroscopy using a DXR Thermo Fisher Scientific Raman spectrometer with a 532 nm laser excitation line, 1.5 mW of power and a spot size of 0.7 µm, and transmission electron microscopy using a Jeol JEM 2010 microscope. The accelerating voltage was 200 kV.

For the size calculation using the BPM, from the Raman spectra, a difference with the maxima of the peak of the Si-nc and the bulk Si (521 cm\(^{-1}\)) \[15, 16\] was calculated, then the equation \[13\]:
was solved for the diameter of the Si-nc. Where $\omega(L)$ is the frequency of the Raman phonon in a nanocrystal with size $L$, $\omega_0$ is the frequency of the optical phonon at the zone center, and $a$ is the lattice constant of Si.

For the PCM, the Raman spectra of the Si-nc are normalized and fitted using a cubic polynomial function; afterwards, the spectra are fitted by means of an integral of a Lorentzian distribution function according to the described in reference [14]. The obtained data are then used to estimate the Si-nc diameter. The equation used for the size estimation is shown below:

$$
I(\omega) = \int_{D_{\text{min}}}^{D_{\text{max}}} \Phi(D) \frac{L(\omega, D)}{D} dD
$$

where

$$
L = \frac{A(D)}{\pi} \frac{\Gamma_{\text{NC}}(D)}{\sqrt{\omega - \omega_{\text{NC}}(D)}} + \frac{\Gamma_{\text{NC}}(D)}{2}
$$

$$
A(D) = 1.4 \times 10^{-2} D^{-3}
$$

$$
\Gamma_{\text{NC}}(D) = \Gamma_{\text{Si}} + 60 \times D^{-4}
$$

$$
\omega_{\text{NC}}(D) = \omega_{\text{Si}} - 34.8 \times D^{-2}
$$

$$
\Phi(D) = \frac{1}{\sigma D \sqrt{2\pi}} \exp\left\{-\frac{\log\left[\frac{|D/D_0|^2}{2\sigma^2}\right]}{2\sigma^2}\right\}
$$

$A(D)$ represents the peak intensity, $\Gamma_{\text{NC}}(D)$ the FWHM and $\omega_{\text{NC}}(D)$ the peak position.

**Results and discussion**

Figure 2 shows the Raman spectra of the colloidal Si nanoparticles obtained from the ablation of the Si target in water for 5 and 10 min at different fluences. The inset on the figure shows the sizes calculated with the theoretical models, table 1 shows the experimental conditions for the ablation experiments as well as the liquid media and the calculated sizes for the Si-nc using the PCM and BMP models. As it can be seen, the Raman spectra for Si consist in a peak in the form of a Cauchy-Lorentz distribution. For Bulk Si, the peak is centered at 521 cm$^{-1}$ and for the colloidal Si-nc samples a shift to lower frequencies and a peak broadening can be observed. This is a consequence of the Si-nc phonon quantum confinement induced by size reduction to the nanoscale [13, 14]. As it can be seen in figure 2, for our experiments regarding the use of water as liquid medium, there is a trend in which the lower the fluence and the higher the time, the higher is the shift compared to Bulk Si; and thus, the size of the silicon nanocrystals is smaller. Figure 3 shows the nanoparticles size as a function of the fluence for BPM (top) and PCM (bottom) models; as it can be seen, at lower fluence, the size of the nanoparticles is smaller regardless the liquid media. Furthermore, it can be seen that ablation at a lower wavelength in ethanol, smaller nanoparticles can be obtained as compared to ablation at 1064 nm. However, this behavior will strongly depend
on laser parameters and liquid media, and thus more experiments will be needed to confirm any general trend, which is out of the scope of the present research.

Figure 4 shows Raman spectra corresponding to two different regions of the sample obtained using a fluence of 0.608 J cm\(^{-2}\). For region 1 a deconvoluted Raman spectrum is shown. As it can be seen, there are bands centered at 490 and 513 cm\(^{-1}\). The band at 490 cm\(^{-1}\) corresponds to amorphous Si\[^8\]. Semaltianos et al\[^7\] reported a shift on the TO Raman mode of Si attributed to phonon confinement, they also found that the band centered at 490 cm\(^{-1}\) can be associated to amorphous Si\[^6\]. The band centered at 513 cm\(^{-1}\) is associated to Si-nc. The band corresponding to region 2 is centered at 513 cm\(^{-1}\), which indicates that a major contribution of

| Fluence (J/cm\(^2\)) | Liquid medium | Time (min) | Wavelength (nm) | BPM (nm) | BPM error | PCM (nm) | PCM error |
|----------------------|---------------|------------|-----------------|----------|-----------|----------|-----------|
| 0.687 | Water | 5 | 1064 | 3.74 | 0.26 | 4.35 | 0.23 |
| 0.687 | Water | 10 | 1064 | 2.81 | 0.19 | 3.32 | 0.22 |
| 0.608 | Water | 10 | 1064 | 2.13 | 0.07 | 2.32 | 0.10 |
| 0.530 | Water | 10 | 1064 | 2.06 | 0.07 | 2.64 | 0.14 |
| 0.687 | Water | 5-LT | 1064 | 3.36 | 0.08 | 3.62 | 0.31 |
| 0.687 | Water | 10-LT | 1064 | 5.09 | 0.25 | 5.63 | 0.27 |
| 0.608 | Water | 10-LT | 1064 | 6.73 | 0.51 | 11.04 | 0.10 |
| 0.530 | Water | 10-LT | 1064 | 6.73 | 0.26 | 5.92 | 0.11 |
| 0.687 | Ethanol | 10 | 1064 | 4.24 | 0.10 | 3.20 | 0.20 |
| 0.608 | Ethanol | 10 | 1064 | 4.43 | 0.17 | 3.28 | 0.23 |
| 0.530 | Ethanol | 10 | 1064 | 1.65 | 0.01 | 2.01 | 0.10 |
| 0.530 | Ethanol | 10-LT | 1064 | 1.22 | 0.04 | 2.00 | 0.10 |
| 0.687 | Ethanol | 10 | 532 | 3.66 | 0.08 | 2.04 | 0.35 |
| 0.608 | Ethanol | 10 | 532 | 5.03 | 0.38 | 2.61 | 0.31 |

Figure 3. Sizes of the Si-nc as a function of the ablation obtained with the BPM (top) and PCM (bottom) models.
crystals can be found at that zone. The position of this band agrees with the band found in region 1. The deviation found in this spectrum as compared to the spectra of the other samples at different fluences could be a consequence of change in the nanocrystals morphology. It is known that the ablation mechanisms can induce different morphologies \cite{11} and thus, different Raman signal shifts. For example Liu et al\cite{17} reported similar Raman shifts for silicon micro and nanocubes.

The crystallization mechanism of the semiconductor nanocrystals involves extreme thermodynamic conditions occurring during the ablation process \cite{11}. Irradiation with high energy nanosecond pulses of a target produces the melting and evaporation of the surface, leading to a plasma expansion into the liquid, the pressure and temperature produced in the process are high enough to modify the structure of the particles; also, thermal quenching plays an important role on the crystalline structure of the obtained silicon nanocrystals \cite{4, 12}.

Figure 5 shows the Raman spectra of the laser irradiated colloidal Si in water. The inset on the figure shows the sizes calculated with the theoretical models. The laser treated nanoparticles are bigger than the non-treated. According to the literature, this means that laser melting (LM) was induced instead of laser fragmentation \cite{11, 12}. However, in the sample irradiated for 5 min there is a laser fragmentation since the crystals reduced their size from 4 to 3 nm. Thus, using laser post-treatment size selectivity can be achieved. The apparent discrepancy in size for the sample irradiated at 608 J/cm\textsuperscript{2} (also showed in figure 3), arises from the fact that PCM considers both width and peak position, and this sample is composed of amorphous material as well as nanocrystals with two size distributions.
Figure 6 shows the Raman spectra of the Si target ablated in ethanol for 10 min at different fluences and a laser treated sample using a 1064 nm wavelength. The inset on the figure shows the sizes calculated with the theoretical models. As it happened with the water samples, a peak shift and broadening can be observed due to size reduction. The lower the fluence the higher is the shift as compared to bulk Si, and thus the size of the silicon nanocrystals decreases for decreasing fluence. It is worth noting that the shift of the spectrum corresponding to the sample obtained from the laser treatment is large, which, according to the limits calculation of the models [13, 14], cannot correspond to quantum confinement in nanocrystals. Instead, this shift is attributed to the existence of amorphous silicon [6, 7]. To further analyze this behavior, a deconvolution of the spectrum corresponding to the laser treated sample is shown in figure 7. Notice that the spectrum is composed of three signals centered at 498, 506 and 518 cm\(^{-1}\). The band at 518 cm\(^{-1}\) is associated to Si-nc, meanwhile the bands at 498 and 506 cm\(^{-1}\) are associated to amorphous silicon. The explanation of this behavior is due to the existence of a melt-quenching process fast enough to inhibit complete crystallization of the particles.

Figure 8 shows the Raman spectra of the colloidal Si nanoparticles ablated in ethanol for 10 min at different fluences using a 532 nm wavelength. The inset on the figure shows the sizes calculated with the theoretical models. As it can be seen a shift and broadening can be observed because of the size of the Si-nc. In this case, and compared to figures 2, 4 and 6 the shift is larger for higher fluences.

For the Si-nc in ethanol, it can be shown that ablating with 1064 nm gives smaller Si-nc sizes than when 532 nm is used, this is because the absorption coefficient of Si, at 532 nm is higher than the absorption coefficient at 1064 nm [18]. Comparing results obtained using the same fluences at different wavelengths, we can see in the...
present experiments, that ablation with the 1064 nm produces smaller nanoparticles for lower fluences, meanwhile for ablation with 532 nm; higher fluences are needed to get smaller nanoparticles. In order to confirm the results regarding the crystal size, transmission electron micrographs were recorded.

**Figure 8.** Raman spectra of the colloidal Si nanoparticles ablated in ethanol for 10 min at different fluences using a 532 nm wavelength.

**Figure 9.** TEM micrograph corresponding to the sample obtained using a fluence of 0.687 J cm\(^{-2}\) in water during 10 min using a 1064 nm wavelength. The inset shows a histogram of the nanoparticles.
Figures 9 and 10 show representative TEM images of Si nanoparticles in water and ethanol, respectively. The inset in figure 10 shows selected area electron diffraction pattern were the crystalline structure of the particles can be observed. For the case of Si–nc in water (figure 9) a distribution of particles ranging from 2 to 5 nm can be observed and agrees with calculations from Raman spectroscopy data in which we obtained medium sizes of 3.32 nm with the PCM model and 2.81 nm with the BMP model, as it can be seen in the inset of figure 9, there is a major distribution of nanoparticles of that size. The size, shape and distribution of colloidal nanoparticles synthesized by laser ablation depend on the confining media and the laser energy, wavelength, etc Liu et al [19] reported the synthesis of 40–60 nm Si nanoparticles produced by a 10 ns pulse laser with a wavelength of 532 nm with a wide distribution of sizes and the presence of microparticles.

For the case of Si–nc in ethanol (figure 10) amorphous particles from 20 to 50 nm can be observed. However, the inset in figure 10 shows the presence of well-defined diffraction rings together with a diffuse background, which confirms the presence of a mixture of nanocrystalline together with amorphous silicon as it was observed by Raman spectroscopy.

Conclusions

Colloidal Si nanoparticles were synthesized by low fluence laser ablation of solid Si in water and ethanol. Nanocrystals ranging from 2 to 11 nm where found using BPM and PCM models and confirmed by TEM. Using theoretical models is a fast and reliable method to analyze a large amount of samples, thus Raman Spectroscopy is suitable for analyzing particles produced by LAL. For the case of Si-nc in water at 1064 nm the lower the fluence the smaller the size of the nanocrystals. Laser treatment of the colloids can be used to achieve size selectivity. For the case of Si-nc in ethanol it was found that using a laser wavelength of 1064 nm, the lower the fluence the smaller the size of the Si-nc, whereas using 532 nm, the lower the fluence the bigger the size of the nanocrystals.
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