Raman diagnostics of silicon nanocrystals dissolution in aqueous medium

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Abstract: Raman scattering in ensembles of silicon (Si) nanocrystals (NCs), which were prepared by different methods and then stored in an aqueous medium, was studied to reveal features of the Si NC dissolution process. Arrays of crystalline Si nanowires, mesoporous Si nanoparticles and spherical Si NCs have been analyzed after exposure in water during dialysis for elimination of the dissolution products from the medium. According to the one-phonon Raman spectroscopy the Si nanowires with cross-section size of the order of 100 nm were resistant to the dissolution process both in water and physiological saline for 2 weeks at least. The storage of mesoporous Si nanoparticles in water for 1 day resulted in a strong decrease of the Raman intensity and a low energy shift of the Raman spectrum, which was explained by size reduction of Si NCs below 10 nm. Si NCs with the initial size distribution from 5 to 100 nm after exposure in water during 24 hours revealed a decrease in the contribution of small NCs that narrowed the size distribution. The obtained results can be used in order to choose appropriate type of Si NPs for biomedical applications.

Keywords: silicon nanocrystals, nanowires, porous silicon, Raman scattering, biodegradation

1. Introduction

In recent years, various types of silicon (Si) nanocrystals (NCs) and nanoparticles (NPs) have been extensively studied for applications in biomedicine, including both the diagnostics and therapy (theranostics) of cancer [1, 2]. Laser-ablated Si NPs [3] and porous ones formed by electrochemical method [4-8] exhibit unique physical and chemical properties, which can be used for the theranostics of cancer [2, 4, 6, 7]. For example, Si NPs can act as sensitizers for sonodynamic [6, 7], photodynamic [8, 9] and photothermal [10] therapy modalities as well as for the radio-frequency electromagnetic hyperthermia [11] of cancer both in vitro and in vivo. It is found that Si NPs reveal properties of contrast agents for optical [3-5] and magnetic resonance [12] bioimaging. Photoluminescence (PL) of laser-ablated Si NCs with sizes of 3-5 nm was shown to be efficient in cancer cells in vitro [3]. Bioimaging studies with detection of the PL and Raman signals from porous Si NPs were used to monitor processes of the uptake and biodegradation (dissolution) of NPs in cancer cells in vitro [5].
In our work Si NPs, which were prepared by different chemical and physical methods, were stored in aqueous media and then they were investigated by means of the Raman spectroscopy in order to reveal features of the dissolution process.

2. Samples and Methods
Experiments were carried out with samples of Si nanowires (NWs) grown on crystalline Si (c-Si) substrates, mesoporous Si (meso-PSi) NPs and non-porous Si NCs. Figure 1 shows typical images of the samples in a transmission electron microscope (TEM).

Si NWs were formed by using metal-assisted chemical etching (MACE) of boron doped (100)-oriented c-Si wafers with specific resistivity of 1-10 Ω-cm. The MACE process has been done in two steps [13]. At the first step, silver (Ag) NPs with mean sizes 20-100 nm were deposited on the top of c-Si substrates by using the chemical reduction of silver nitrate (AgNO₃) in a solution of hydrofluoric acid (HF) [14]. Afterwards, the c-Si substrates with deposited Ag NPs were etched in a mixture of HF and hydrogen peroxide (20%) in water that resulted in heterogeneous Ag NP-assisted etching of c-Si, which was transformed into Si NW arrays [13, 14]. Then residual Ag NPs were removed by etching in concentrated nitric acid and the Si NWs on c-Si substrates were carefully washed in de-ionized water.

Figure 1a shows a TEM image of the prepared Si NWs detached from the substrate and deposited on a carbon grid. One can see from the figure that the NWs have cross-sectional size (diameters) about 20-100 nm. The length of SiNW was controlled by the time of the second step of MACE and it was about 10-15 µm for the investigated samples. The prepared NWs on c-Si substrates were immersed in de-ionized water or in saline (aqueous 0.9% NaCl solution). Prior to Raman measurements the samples were removed from the solution and they were dried in air at room temperature for 20 min.

![TEM images of (a) Si NWs, (b) meso-PSi NPs and (c) Si NCs.](image)

Samples of meso-PSi were prepared by standard electrochemical etching of heavily boron-doped c-Si wafers with surface orientation (100) and specific resistivity of 1-5 mΩ-cm in a solution of HF and ethanol (HF(50%):C₂H₅OH=1:1) at etching current density of 60 mA/cm² for 1 h (see, for example [4]). The prepared meso-PSi films with thickness about 70 µm were separated from c-Si substrates by a short increase of the current density up to 600 mA/cm². Aqueous suspensions of meso-PSi NPs were obtained by mechanical grinding of meso-PSi films mixed with de-ionized water. The grinding was done by using a planetary ball mill FRITSCH “Pulverisette 7” with zirconium oxide mill vessel and balls (diameter of 5 mm) at rotation speed of 800 rpm for 9 minutes. According to the TEM data (Figure 1b) as-prepared meso-PSi NPs are characterized by mean size of about 50-100 nm in agreement with previously reported results [4]. It is seen from Figure 1b that the meso-PSi NPs have porous structure and they consist of agglomerates of Si nanocrystals with smaller sizes.

Plasma-synthesized Si (pl-Si) non-porous NPs were prepared by microwave plasma-assisted ablation/fragmentation of microcrystalline Si powder (99.9%) in inert gas atmosphere (see for details Ch. 5 in [1]). The TEM study shows that initial pl-Si NPs consist of nearly spherical Si NCs with sizes in the range from 5 to 100 nm (see Figure 1c).
The dissolution of NPs of meso-PSi and pl-Si in aqueous medium was studied for the samples with initial concentration about 1 g/L, which were put in dialysis bags with pore sizes of 6-10 kD and kept for 1 to 24 hours in distilled water at room temperature. Then, at intervals 1, 2, 3, 6, 12, 24 hours, drops of the suspension were taken and deposited on stainless steel substrates and then they were dried in air for 10-15 min.

Raman spectra of the dried samples were measured by using a double grating DFS-52 spectrometer (LOMO, Russia) in a 90-degree scattering geometry. A cooled photomultiplier FEU-79 served as the detector. The source of excitation radiation was an argon laser with wavelengths of 488 and 514.5 nm and excitation intensity on the sample was limited to 100 W/cm² to avoid the laser-induced heating. To measure the Raman spectra with excitation at the wavelength of 632.8 nm, a micro-Raman spectrometer Horiba Jobin Yvon LabRAM HR Visible was used.

3. Results and Discussion

Figure 2 shows the Raman spectra of the initial sample of SiNWs and those stored in water or in saline. The spectra consist of a sharp line at 520.5 cm⁻¹ with FWHM (full width at half maximum) of about 3-4 cm⁻¹, which corresponds to the scattering by optical phonons of the crystal lattice of Si. The high intensity line in comparison with c-Si substrate indicates an enhanced interaction of the exciting radiation with SiNWs due to the multiple scattering. The line shape of the Raman spectra of the both c-Si and SiNWs is well described by the Lorenz function:

\[ I_c(\omega) = \frac{C}{(\omega - \omega_c)^2 + (\Delta \omega_c)^2}, \]

where \( \omega_c = 520.5 \text{ cm}^{-1} \) is the Raman phonon frequency in c-Si, \( \Delta \omega_c = 3 \text{ cm}^{-1} \) is the width of the Raman line of c-Si at room temperature, and \( C \) is a constant.

It was found that exposure of SiNWs in aqueous solutions for 2 weeks at least did not lead to a significant change in line shape (see Figure 2), indicating the immutability of the dimensions of nanowires. The reason for this fact can be the significant size of the cross section of SiNWs and sufficient quality oxide layer on the surface of SiNWs formed at the final preparation stage.

![Figure 2](image)

**Figure 2.** Raman spectra of SiNWs before (thick solid line) and after storage in water (dashed line) and saline (dotted line) for 2 weeks as well as for c-Si substrate (thin solid line), for comparison.

Figure 3 shows Raman spectra of meso-PSi NPs before (as-prepared) and after storage in water (in dialysis regime). Note that the Raman scattering intensities for these samples were rather low relative to the signal from undoped c-Si wafers that can be explained by the Fano effect due to a significant number of equilibrium charge carries (holes) in meso-PSi [15]. The meso-PSi NPs before storage in water exhibit an asymmetric line with maximum at 518 cm⁻¹, full width half maximum about 8-9 cm⁻¹ and a shoulder in the low frequency part of the spectrum. Such form of the Raman spectrum indicates
an effect of the phonon confinement in Si NCs with sizes about 5 nm [16]. Beside the NC line the spectrum consists of a week and broad band with maximum at 480 cm\(^{-1}\), which is typical for amorphous silicon (a-Si) [15]. Indeed, a certain part of meso-PSi NPs can be amorphous due to the procedure of mechanical grinding in water, which was used for the NP preparation.

To fit the Raman spectra of meso-PSi we use a model proposed in Ref.[17]. According to the model the Raman spectrum of Si NCs is described by the following equation [16,17]:

\[
I_{NC}(\omega) = \int_0^1 B \cdot \exp\left(-\frac{1}{2} q^2 L^2\right) d\omega \cdot dq,
\]

(2)

where \(\omega_c = 520.5 \text{ cm}^{-1}\) is the Raman phonon frequency in c-Si, parameter \(L = d/a_0\), \(d\) is the diameter of NC, \(a_0 = 0.543 \text{ nm}\) is the lattice constant of c-Si, \(q\) is the phonon wave vector expressed in \(2\pi/a_0\) units, and \(\omega_c(q) = \omega_c(1-0.18q^2)\) is the phonon dispersion relation in c-Si [17]. \(B\) is a constant.

Note, that Equation 2 well describes the phonon confinement in spherical Si NCs with sizes 1-10 nm [16], while for the Raman scattering from larger NC one can simply use Equation (1).

The Raman spectrum of a-Si is described by the following relations [17]:

\[
I_A(\omega) = A \cdot \exp\left(-\frac{(\omega - \omega_c)^2}{2\delta^2}\right),
\]

(3)

where \(A\) is a constant, \(\omega_c = 480 \text{ cm}^{-1}\) and \(\delta = \Gamma\left(2\sqrt{2\ln 2}\right)^{-1}\), \(\Gamma = 70 \text{ cm}^{-1}\) are the position of the peak and its width at half maximum, respectively.

It is assuming that the Raman scattering from the investigated sample consists of contributions of all fractions (phases), i.e. NCs with size above 10 nm without phonon confinement (c-Si-like fraction), small Si NCs with phonon confinement and a-Si fraction, and it can be given by the following expression:

\[
I_{\text{Sum}}(\omega) = I_C(\omega) + I_{NC}(\omega) + I_A(\omega).
\]

(4)

The volume fraction of each phase can be estimated as a ratio of the corresponding integrated intensity to the total Raman spectrum, e.g. \(f_{NC} = \int I_{NC}(\omega) d\omega / \int I_{\text{Sum}}(\omega) d\omega\).

Fitting of the Raman spectra of meso-PSi by using Equations (1)-(4) shows that the mean size of Si NCs accounts 5 nm and it remains nearly the same for as-prepared NPs and stored in water ones, while contribution of the Si NCs becomes smaller and the a-Si fraction increases (see Figure 3). The latter indicates additional disordering of the crystal lattice of Si NCs due to their partial dissolution in water in agreement with [5].

Figure 3. Raman spectra of as-prepared meso-PSi NPs (open circles) and those after 1 day storage in water (filled circles) and fits (lines) of the corresponding spectra by using Equations (1)-(4).
Figure 4 shows Raman spectra of pl-Si samples before and after storage in water (dialysis). The spectrum of the initial sample is asymmetric with maximum at 520 cm\(^{-1}\) and a width of 8 cm\(^{-1}\) that indicates the presence of Si NCs with a wide size distribution from 5 till 100 nm in agreement with the TEM data (see Figure 1c). Upon exposure of the samples in water for 1 hour a significant decrease in the intensity and change of the spectrum of Raman scattering occurred, which can be explained by dissolution of part of the NCs and the change in their size distribution. The sample stored in water for 24 h exhibited a strong decrease in the intensity of Raman scattering, and the position (520 cm\(^{-1}\)) was similar to that for c-Si substrate. This fact indicates almost complete dissolution of small NCs with sizes below 10 nm, while NSs with large sizes remained. Indeed, in the TEM image of pl-Si show NPs with sizes of about 100 nm (see Figure 1c), which do not subject to significant reduction of their size during a one day in water. On the one hand the latter fact is similar to the stability of SiNWs (see Figure 1a). On the other hand, the crystal lattice defects and/or large specific surface area, which are inherent for small pl-Si NPs, are possible reasons for their rapid dissolution in water as it was observed in the Raman scattering measurements (see Figure 4).

![Figure 4. Raman spectra of pl-Si samples before (open circles) and after storage in water for 12 h (stars) and 24 h (up-triangles). The spectra are fitted by Equations (1)-(4) (I\(_{\text{sum}}\), thick solid lines), while the fractions of NCs (I\(_{\text{NC}}\)), amorphous (I\(_{A}\)) and crystalline (I\(_{C}\)) phases of Si are plotted by thin solid, dashed and dotted lines, correspondingly. The curves are translated in the vertical direction for better representation.](image)

4. Conclusions
The Raman spectroscopy studies of three types of nanocrystalline silicon samples with different nanocrystal sizes and morphologies, i.e. crystalline nanowires, mesoporous nanoparticles and spherical non-porous ones, were carried out to reveal features of their dissolution in aqueous media. The nanowires formed by metal-stimulated etching of c-Si, were found to be resistant to the dissolution both in pure water and in saline solution for 2 weeks at least. It can be explained by the crystal structure, relatively large cross-sectional size about 100 nm and the oxide-coated surface quality. In the series of experiments with meso-PSi NPs, it was found that dissolution of the significant part of nanocrystals occurred after the storage in water for 1 day, was accompanied by the increase of the relative contribution of the amorphous silicon phase. As for the non-porous nanoparticles it seems that the nanocrystals with sizes less than 10 nm are almost dissolved within 1 day of storage in water, while nanocrystals with sizes ~100 nm are retained. The obtained results allow us to choose an appropriate type of Si nanostructures for biomedical purposes. In particular, silicon nanowires, because of their stability in aqueous medium, can be recommended for use as active elements of biosensors or biomarkers in biochemical sensors. Nanoparticles of mesoporous Si as quickly biodegradable material can be used for express therapy of various diseases, e.g. hyperthermia of
cancer. As for the non-porous nearly spherical Si nanoparticles, which exhibit the strong Raman scattering even after one-day storage in water, can be considered as an agent for the simultaneous optical diagnostics and therapy (theranostics).

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