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Preparation of luminescent and optical limiting silicon nanostructures by nanosecond-pulsed laser ablation in liquids

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ABSTRACT

Pulsed laser ablations of a silicon rod target in water, hydrogen peroxide water solution and ethanol were performed, varying the laser parameters. The structural and compositional characteristics of the nanoparticles were studied by photoluminescence, micro-Raman, TEM and X-ray photoelectron spectroscopy. A significant change of the nanoparticle structure and of its interface was observed, depending on the solvents used. Mainly very small nanoparticles are formed in all cases. A wide range of crystalline fractions and chemical compositions has been produced by properly modulating the ablation parameters. Even if a weak photoluminescence behaviour has been obtained in almost all the examined cases, a significant nonlinear optical response has been probed by Z-scan technique. The calculated third order refractive index and absorption coefficient are found to be weakly affected by the specific ablation process, and hence almost independent from the structural and compositional characteristics of the nanoparticles. The only marked difference is observed in the comparison between silicon/silicon oxide nanoparticle and pure silicon nanoparticles, the latter being produced in ethanol. More specifically, a one order of magnitude higher refractive index is observed with nanoparticles dispersed in ethanol.

1. Introduction

In the past decades nanostructured silicon has generated large interest as a promising key material to establish a Si based photonics. Generally, silicon has been regarded as unsuitable for light emitting devices due to its indirect optical transition, though it is the most important material in semiconductor device fabrication. However, visible light emission from low-dimensional Si-based materials, such as highly porous Si, have been largely investigated since these low-dimensional materials exhibit a quasi-direct band gap as a result of quantum confinement of electron and hole wavefunctions [1]. By controlling the size of the particles, the confinement potential can be modified and, consequently, their emission can be appropriately tuned. Moreover, the low absorption coefficient makes nanocrystalline silicon (nc-Si) attractive as active medium in waveguide structures. Besides an efficient visible emission, silicon of nanometer size shows a largely enhanced nonlinear polarizability, which indicates that nanosized silicon should be a promising nonlinear optical material usable for all-optical switching devices [2–4]. The optical nonlinearity of nanosized silicon varies for different preparation methods and experimental conditions. In particular the results, currently reported in literature [5], reveal that the nonlinear optical response of the nanomaterial depends on the surrounding matrix.

Although self-assembly of nanocrystalline silicon structures has been reported [6–13], nevertheless a reliable fabrication technique capable of producing very small silicon nanocrystals surrounded by a tailored oxide shell and showing optical limiting functionality, still remains a challenge.

In this work, the results of a laser-induced ablation of a silicon target in three different liquid environments, that is pure water, hydrogen peroxide water solution and pure ethanol, are described and discussed. We analyzed the structural, compositional, linear and nonlinear optical characteristics of the nanoparticles. In particular, to our knowledge, this is the very first investigation of nonlinear optical response of silicon nanostructures prepared by nanosecond-pulsed laser ablation in liquids (PLAL).

2. Experimental

Pulsed laser ablation of a silicon rod target in pure water (H_2O), hydrogen peroxide 30% (H_2O_2) water solution and pure ethanol (CH_3CH_2OH) has been carried out using the second harmonic (532 nm) of a Nd:YAG laser operating at 10 Hz repetition rate with a pulse width of 5 ns. The target was irradiated with a laser fluence of 1.5 J cm^{-2} and 7 J cm^{-2} for typical irradiation times of 10 min and 30 min. The ablation in the H_2O_2 solution was carried out only at low fluence and for 10 min time.

The photoluminescence (PL) and the micro-Raman responses of the nanocrystals were investigated in the colloidal phase immediately after the ablation process.

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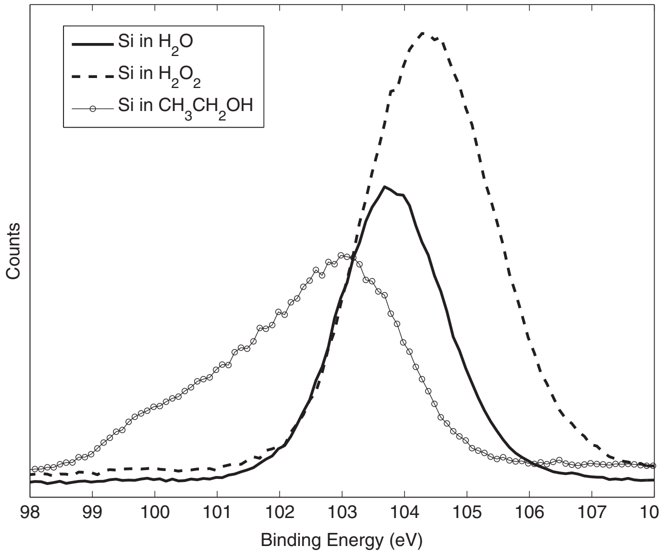

Fig. 1. Si 2p XPS spectra of silicon nanoparticles on Si substrate.

For the PL measurements an excitation wavelength of 300 nm was used, obtained from the monochromated output of a Xe lamp. A fraction of the same colloids was deposited on proper substrates to carry out a Transmission Electron Microscopy (TEM) characterization. TEM images were taken by a JEOL JEM-2010 microscope operating at an accelerating voltage of 80 kV. The chemical composition of the films, deposited by spraying on different substrates, has been investigated by means of X-ray Photoelectron Spectroscopy (XPS) using a K-Alpha system from Thermo Scientific equipped with a monochromatic Al-Kα source (1486.6 eV) and operating in CAE mode with a pass energy of 50 eV.

Raman spectra on colloids were excited by the 632.8 nm radiation of an He–Ne laser. The backscattered radiation, collected by an Olympus BX 40 microscope optics using a 10× Mitutoyo infinity-corrected long working distance objective lens, was analyzed by a Jobin Yvon 1800 mm^{-1} monochromator equipped with a LN_2 cooled CCD sensor.

The nonlinear optical properties were determined by the Z-scan method [14] using a pulsed Nd:YAG laser (wavelength 532 nm, 5 ns pulse duration, 1–10 Hz repetition rate). The incident laser beam was divided by a beamsplitter: the reflected part was taken as reference beam, the transmitted one was focused, with a 300 mm focusing lens, into a 1 cm length quartz cuvette. The optical limiting measurements were carried out by moving the sample along the axis of the incident beam (Z direction) with respect to the focal point and keeping constant the laser pulse energy. The sample and the reference beam intensities were detected simultaneosly with a dual channel energy meter. The measurements were taken both in open and closed configurations, to evaluate the third-order nonlinear susceptibility $\chi^{(3)}$ by determining the nonlinear refractive index n_2 and the nonlinear absorption coefficient β. In the closed aperture configuration a finite aperture (d = 400 μm) was placed at 250 mm from the focal point. The focused beam size was 200 μm with a pulse energy of 5 mJ.

3. Results and discussion

3.1. XPS analyses

XPS was the experimental technique adopted to study the specific bonding configurations present and their relation with the selected process in order to monitor the composition of the silicon nanoparticles surrounded by an oxide shell. In Fig. 1 the Si 2p photoelectron spectra for the three samples prepared at low ablation fluence are shown. Generally, the Si 2p bands of a silicon oxide film show the presence of two distinct components at about 99.5 eV (Si^0) and at about 104 eV (silicon atoms bonded to oxygen, that is Si^{4+}). In our case, we looked at the modifications occurred in the subband structure of the Si 2p peaks as a function of the adopted solvent. Each spectrum has been fitted with three components, that is a metallic silicon contribution, a Si–C one and an oxidized silicon one. The results of the deconvolution are reported in Table 1. A readily recognizable modification of the Si 2p peaks is evident. Almost negligible metallic like silicon and Si–C contributions can be seen for ablation performed in H_2O and in H_2O_2 water solution. Instead, the spectrum from the silicon colloid in ethanol clearly shows a significant metallic silicon contribution even if the ratio against the oxide silicon phase is relative low. Moreover a clear Si–C derived component is highlighted. Based on a nanoparticle core/shell model and taking into account that XPS probes only a surface layer thickness comparable with the inelastic mean free path of the escaping electron in SiO_2 (λ = 2.45 nm) [15,16], it is plausible that the outmost oxide shell in the case of ethanol solvent is thinner than about 2.5 nm while nothing can be said for the shell thickness in the other two cases (H_2O and H_2O_2), except that it must be larger than about 3 nm. Moreover, the evident chemical shift of the oxidized silicon contribution suggests that the average stoichiometry of the oxide shell tends to completion (SiO_2) as the oxygen availability in the ablation liquid increases. In fact, the binding energy of the Si 2p photoelectron in silicon suboxides (SiO_x, $1 < x < 2$) increases from about 100.2 eV up to 104.2 eV with about 1 eV step on increasing the valence state from 1 to 4, being the latter position that of the full stoichiometric case [17]. The position of the oxidized silicon contribution shifts from 103.1 eV, in the case of ablation in ethanol, to 103.8 eV in the case of ablation in pure water, up to 104.4 eV in the case of ablation in hydrogen peroxide solution. This observation reflects the oxygen availability in the three solvents. The fully stoichiometric silicon oxide (Si^{4+} valence state) is observed only in the case of ablation in hydrogen peroxide solution, that is the oxygen richest liquid. A mixture of lower valence suboxides is observed in the other two cases. The spectrum from the ethanol colloid shows also a significant shoulder at about 101.3 eV that can be assigned to a Si–C bonding contribution. An examination of the C 1s band (not shown), located in the 280–290 eV binding energy (BE) range, shows the presence of significant C–O bonds (around 286.5 eV BE) and, in the case of Si in ethanol colloid, the appearance of a contribution at about 283.5 eV which is assigned to C–Si bonding configurations, that again suggests the occurrence of some surface carbidization of the silicon nanoparticles, even if to a small extent.

Table 1
Energy and atomic percentage obtained after fitting of XPS spectra collected for samples prepared at low ablation fluence and short ablation time.

Sample	Parameter	Si^0	Si–C	Si–O_x
Si in H_2O	Binding energy (eV)	99.87	100.97	103.81
	At%	0.56	0	99.44
Si in CH_3CH_2OH	Binding energy (eV)	99.96	101.3	103.09
	At%	12.11	24.24	63.65
Si in H_2O_2	Binding energy (eV)	99.91	101.08	104.40
	At%	1.19	0	98.81

3.2. Raman and TEM analyses

The formation of nanocrystalline silicon was investigated by means of micro-Raman technique. It is known that the crystalline silicon Raman spectrum presents a sharp peak at 521 cm^{-1} with a natural linewidth of about 3.5 cm^{-1} while the amorphous Si and SiO_2 broad contributions fall at 480 and 460 cm^{-1}, respectively (even if the Raman cross section of the SiO_2 phase is very low) [18,19]. In Fig. 2 the Raman spectra of all the silicon colloids prepared at low ablation fluence are shown. The spectra are dominated by the silicon related contributions. Concerning the samples prepared in ethanol and in hydrogen peroxide water solutions, the Raman spectra show a broad band at 480 cm^{-1} and a peak at about 520 cm^{-1}, related to the amorphous and the crystalline silicon phases, respectively. On the contrary, in water colloids the crystalline peak becomes the dominant feature of the spectrum. A deconvolution of the Raman spectra was carried out assuming the presence of three contributions: an asymmetric Gauss–Lorentzian