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Oxidation of silicon nanoparticles produced by nanosecond laser ablation in liquids

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Abstract. We investigated nanoparticles produced by laser ablation of silicon in water by the fundamental harmonic (1064 nm) of a ns pulsed Nd:YAG. The silicon oxidation is evidenced by IR absorption features characteristic of amorphous SiO_2 (silica). This oxide is highly defective and manifests a luminescence activity under UV excitation: two emission bands at 2.7 eV and 4.4 eV are associated with the twofold coordinated silicon, $=SiO\bullet\bullet$.

Keywords: laser ablation, nanoparticles, silicon oxidation, time-resolved luminescence
PACS: 79.20.Eb;81.65.Mq;78.67.Bf;78.30.Am;71.55.Jv;78.47.jd

INTRODUCTION

Since its discovery [1], the photoluminescence (PL) emission from silicon nanocrystals (Si-nc) has attracted a wide interest motivated by the potential use in several application fields (optoelectronics, photovoltaics, bioimaging) [2]. In fact, on decreasing the size the emissivity enhances and the emission photon energy blue shifts as a consequence of quantum confinement (QC) effect of excitons [3]. The optical properties of Si based nanostructured systems critically depend on the surface chemistry; oxidation is one of the most relevant reactions resulting in the production of SiO_2 layers. On the one hand, in the oxidized samples with a diameter below 3 nm the luminescence peak position is not accounted for by the QC [4], on the other hand, the Si/SiO2 interface favors the formation of localized states (defects) that can be involved in the radiative recombination process [5, 6].

The development of production methods successful to control the size and the surface properties of Si nanoparticles is a relevant topic in material science. Laser ablation (LA) in liquids is particularly promising since it is a green method suitable for bio-friendly applications and it provides effective control parameters (laser photon energy, fluence, pulse duration, liquid reactivity) for the morphology and the structure of the related products [7].

In this work we investigate the nanoparticles produced by LA of a Si wafer in water and the effect of their oxidation. Our experimental approach is based on the use of time-resolved luminescence and IR absorption technique to probe the structural properties, thus providing a solid support to discuss the origin of the observed PL bands.

EXPERIMENTAL METHOD

The synthesis of Si-SiO_2 nanoparticles was carried by ns LA in liquids; the setup is sketched in Figure 1. A n-type Si (100) wafer with a thickness of 0.5 mm, used as target, was placed at the bottom of a becker containing 8 mL of de ionized water. The fundamental harmonic of a pulsed Nd:YAG laser (Quanta System SYL 201, =1064 nm, repetition rate 10Hz, pulse width 5 ns) was focused with a lens (150 mm focal length). The laser spot diameter on the target was $\sim$1 mm, and its energy density was $\sim$5 J/cm^2 per pulse, the irradiation time was 45'. During the LA the target was moved by using a rotator stage.

Infrared (IR) absorption spectroscopy was used to investigate the structural properties of our samples. Spectra were acquired by a Fourier-transform spectrometer (Bruker Vertex 70), with a spectral resolution of 0.5 cm^{-1}. They were obtained as difference between the absorption detected in a pellet (thickness of 1 mm) of LA induced nanoparticles dispersed in KBr powder and a reference of KBr.

Time resolved PL spectra were carried out on the colloidal solution in a cell of 1 cm thickness. The excitation was provided by a tunable laser, equipped with an optical parametric oscillator pumped by the III harmonic of a Nd:YAG laser (pulse width $\sim$ 5 ns, repetition rate 10 Hz). The emitted light was spectrally resolved by a grating (150 grooves

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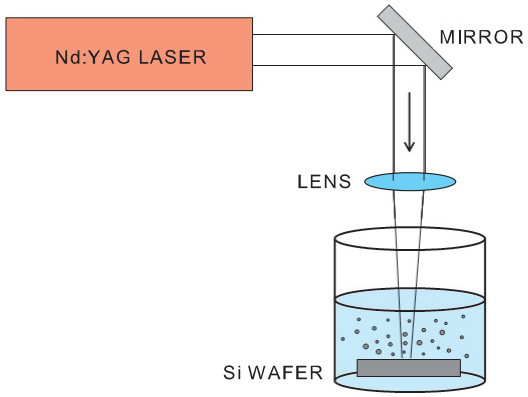

FIGURE 1. Setup used for LA of a Si wafer in water.

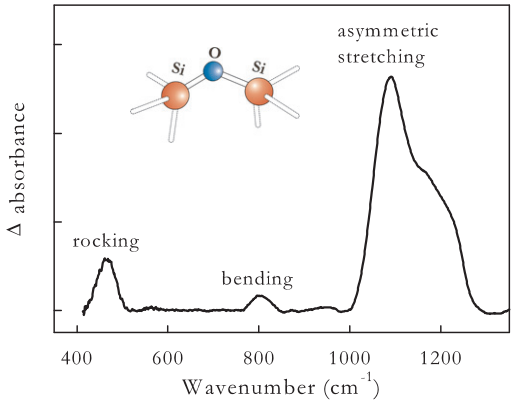

FIGURE 2. IR absorption spectrum of nanoparticles produced by LA of Si target in de-ionized water. Figure adapted from [8].

mm^{-1} and 300 nm blaze), and then acquired by an intensified CCD camera driven by a delay generator (PI MAX Princeton Instruments) setting the acquisition time window, W_T, and the delay, T_D, with respect to the arrival of laser pulses. All the emission spectra were detected with a bandwidth of 10 nm and corrected for the monochromator dispersion. The photoluminescence excitation (PLE) spectra were measured point-by-point by tuning the laser and recording the PL intensity. Each point is normalized to the laser-pulse energy; its value is affected by an uncertainty of $\sim$10% mainly due to the power laser fluctuations.

The luminescence properties were also investigated on a reference sample of oxygen deficient bulk silica $5\times5\times1$ mm^3, containing a known concentration of twofold coordinated silicon defects (10^{16} cm^{-3}).

Results and Discussion

In agreement with previous experiments [8], the colloidal solution produced by LA consists of nanoparticles with an average diameter of a few nanometers and containing Si-nc as demonstrated by the characteristic Raman line at 518 cm^{-1}. We measured the mass of this product after drying the solution; it is $\sim$2.2 mg.

The oxidation of Si-nc leading to SiO_2 production is evidenced by the IR absorption spectrum shown in Figure 2. In the range 400 to 1300 cm^{-1} we observe three bands related to vibrations of the Si-O-Si unit: the rocking mode at 465$\pm$5 cm^{-1}, the bending mode at 803$\pm$5 cm^{-1} and the asymmetric stretching mode at 1090$\pm$5 cm^{-1} with a shoulder

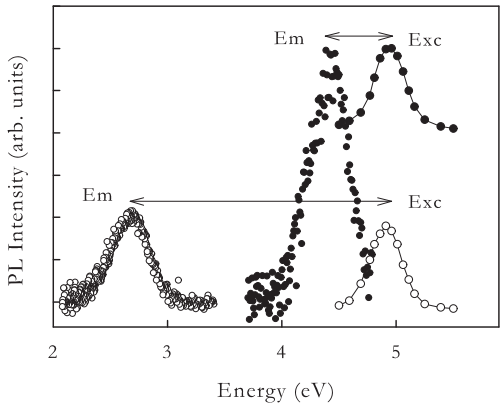

FIGURE 3. Time resolved luminescence detected in the colloidal solution after LA. Symbols represent the emission spectra; symbols and lines represent the excitation spectra.

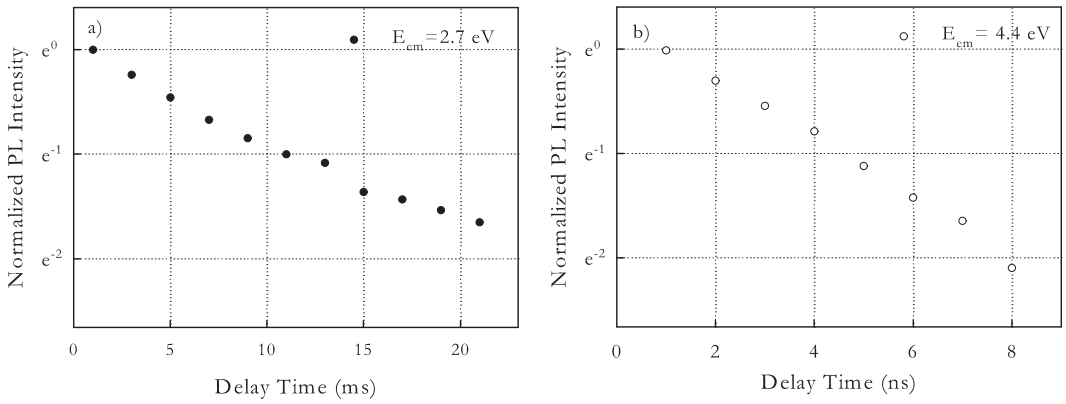

FIGURE 4. Decay curves of the emission at 2.7 eV (a) and at 4.4 eV (b) detected in the colloidal solution under excitation at 4.96 eV. Figure adapted from [8].

around 1200 cm^{-1}.

Time-resolved luminescence experiments help to clarify the structure of LA-produced SiO_2. Under UV excitation two emission bands are observed: the first, acquired with W_T=10 ms and T_D=1 ms, is centered at 2.70±0.04 eV with a FWHM of 0.50±0.05 eV; the second, detected with W_T=10 ns and T_D=1 ns, is peaked at 4.42±0.04 eV with a FWHM of 0.40±0.05 eV. Both emissions have an excitation spectrum consisting of a band peaked around 5.0 eV with a FWHM of 0.35 eV.

The decay curves of these emissions as a function of delay time from the laser pulse are shown in Figure 4; the semilogaritmic scale points out the exponential decay $exp(-T_D/\tau)$. The PL at 2.7 eV is characterized by a slow decay with lifetime $\tau \approx$10 ms; the PL at 4.4 eV has a fast decay with lifetime $\tau \approx$4 ns. These spectroscopic features bring close similarities with the PL observed from an oxygen deficient bulk silica sample containing twofold coordinated Si, =SiO••, with a known concentration of 10^{16} cm^{-3} [9]. Figure 5 reports the time resolved PL spectra acquired in this reference sample with the same experimental conditions used to investigate the LA product. The emission spectrum exhibits as well the bands at 2.7 eV and 4.4 eV, with the same ratio previously reported for the colloidal solution. The decay curves are plotted in the inset: the lifetime is $\tau \approx$10 ms10 ms and $\tau \approx$4 ns for the PL at 2.7 eV and 4.4 eV, respectively.

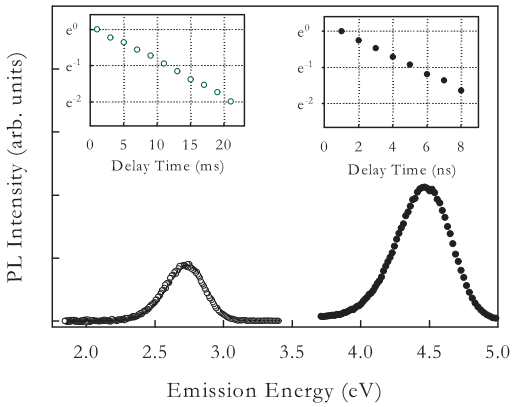

FIGURE 5. Time resolved PL spectra acquired under 4.96 eV excitation in the bulk silica sample. The decay curves of these PL emissions are shown in the insets.

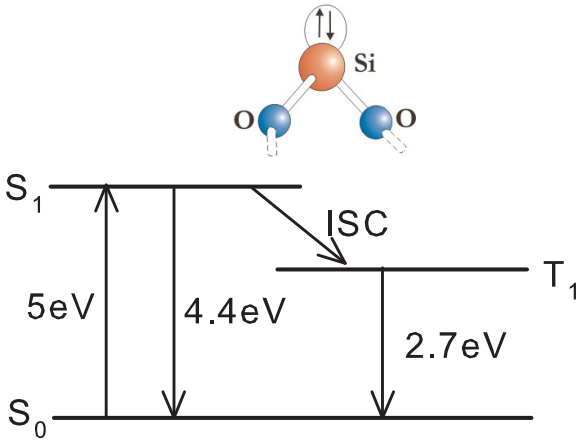

FIGURE 6. Structural model of the two fold coordinated silicon and energy level scheme accounting for the excitation/emission transitions.

Figure 6 sketches the structural model of the twofold coordinated Si with a lone pair in a sp^2 Si orbital [10]. It is worth noting that this defect is peculiar to amorphous SiO2 whereas there is not a counterpart in crystalline quartz. The luminescence lineshape is therefore influenced by the inhomogeneous properties of the glassy matrix [11]. The excitation/emission pathways are accounted for by the energy level scheme shown in the same figure. The emission at 4.4 eV is due to the allowed singlet-to-singlet transition, inverse of the 5.0 eV excitation; the 2.7 eV band is associated with a forbidden triplet-to-singlet transition, its excitation being due to the intersystem crossing (ISC) between the excited singlet and triplet states. We note that this defect is also present at the silica surface with spectroscopic features slightly different from the defect in the bulk. In particular, the ISC rate is more active at the surface than in the bulk, as demonstrated by the different ratio between the 2.7 eV and 4.4 eV PL intensities [12]. Since these characteristics are not observed in our colloidal solution, we rule out the contribution of surface defects. Then, we infer that the PL originates from localized levels of a defect, the twofold coordinated silicon, mainly located in the SiO_2 layer, induced during the oxidation. From the comparison between the PL intensities measured in the bulk reference sample and in the colloidal solution, scaled for the excited volume and the mass, we derive a lower limit of defect concentration in the LA induced oxide (10^{18} cm^{-3}), under the hypothesis that SiO_2 is the main component.

This value, much larger than that measured in native oxygen deficient or in irradiated silica [9], demonstrates that

the oxidation of Si nanoparticles during LA produces a highly defective material with emission properties. As a consequence, the luminescence is a convenient technique to investigate the oxidation processes occurring during or after LA.

In conclusion, 1064 nm ns pulsed LA of a silicon wafer in water produces Si-nanocrystals that undergo an oxidation process resulting in amorphous silica with a high concentration, larger than 1018 cm-3, of twofold coordinated Si. This defect confers luminescence properties to the colloidal solution: a visible band at 2.7 eV and an UV band at 4.4 eV, both excited around 5.0 eV.

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