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Multi-wavelength enhancement of silicon Raman scattering by nanoscale laser surface ablation

A. Merlen[a,*], A. Sangar[a], P. Torchio[b], L.N.D. Kallepalli[c], D. Grojo[c], O. Utéza[c], P. Delaporte[c]

[a] Université du Sud Toulon-Var, CNRS, IM2NP UMR 7334, Bâtiment R, BP 132, F-83957 La Garde Cedex, France
[b] Aix-Marseille Université, CNRS, IM2NP UMR 7334, Campus de Saint-Jérôme – Case 142, F-13397 Marseille Cedex 20, France
[c] Aix Marseille Université, CNRS, LP3 UMR 7341, 13288 Marseille, France

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ABSTRACT

In this paper, we produce nanoholes on a silicon surface by laser ablation. Those nanoholes lead to a yield enhancement of light–matter interaction. Performing Raman spectroscopy on silicon, an enhancement of its main Raman mode is observed: it is twice higher with the nanoholes compared to a flat surface. Such a feature appears whatever the excitation wavelength (488, 514.5 and 632.8 nm) and the laser power, revealing a broad band light–matter interaction enhancement. In addition, no change in the position and shape of the main Raman mode of silicon is observed, suggesting that no structural damages are induced by laser ablation. These results clearly demonstrate the potentiality of such nanostructures for the further development of silicon photonics.

1. Introduction

Trapping light using nanostructures is a powerful approach to improve light–matter interaction. This could lead to many applications, particularly in the field of photovoltaics [1–3]. Nowadays the huge development of optical nano-antennas [4] is an intensive field of research. However the exact interaction between those nanostructures and light is not totally clearly understood due to the multiple interfering mechanisms. In many cases light scattering can be enhanced. This feature has led to the development of surface enhanced spectroscopy, such as surface enhanced Raman spectroscopy (SERS [5]), surface enhanced fluorescence (SEF [6]) or surface enhanced infra-red absorption (SEIRA [7]). For all these techniques, the enhanced optical property of a nanostructured sample is used to detect a signal in conditions where this would normally not be possible due to a weak scattering cross section and a low amount of interacting molecules. For the above-mentioned techniques, the final signal intensity is an experimental sign of the enhanced scattering properties of the nanostructured sample. An enhancement factor (EF) can thus be calculated, even if it is absolutely necessary to be very cautious about its quantitative estimation and its real scientific meaning [5]. These techniques are extremely powerful and single molecule detection has been reported [8–10]. They are usually all based on the giant electromagnetic resonance in the near field of metallic nanostructures due to plasmonic resonance. This is the case for instance with silver, gold or copper nanostructures. Depending on the plasmonic resonance, the intensity of the enhanced signal can thus strongly depend on the wavelength of the excitation and the scattered light. Even if this mechanism leads to a very high enhancement, its plasmonic origin induces a severe limitation: enhancement occurs only if the incoming light wavelength is included in a plasmon absorption band of the nanostructured sample. For broadband optical applications, it is therefore necessary to build plasmonic nanostructures with a broad absorption band, which can require sophisticated protocols (fractal nanostructures, use of a mix of different metals, etc. . .).

Such mechanism is not the only one for the achievement of surface enhanced light scattering and several studies have already reported comparable enhancements without plasmonics. The use of silica microspheres enables also to obtain similar enhancements [11]. The precise mechanism is not fully explained but it appears that an optical resonance based on whispering-gallery mode plays a key role [12]. A lens effect can also occur [13]. In the case of nanostructured silicon (nanoparticles or microcavity) enhancements are also reported [14–16]. A good experimental proof of this effect is the evolution of the main silicon Raman mode. Due to its mechanism, Raman scattering can be considered as an experimental signature of light–matter interaction and is extensively used to study the optical near field enhancement. As a consequence, the light trapping in nanostructured samples induces an increase of Raman modes compared to a flat classical substrate. For silicon, the final intensity of its main Raman mode can therefore be considered as an experimental and quantitative proof of light trapping efficiency. Such specificity is of considerable interest for the development of silicon nanophotonics, in particular for photovoltaics.

* Corresponding author.
E-mail address: merlen@univ-tln.fr (A. Merlen).

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Among all nanostructure architectures giving rise to an enhancement of light–matter interaction, the nanoholes appear as extremely promising [17]. In this paper we report Raman signal enhancement from silicon nanoholes. The silicon nanoholes are realized through laser ablation using silica nanospheres preliminarily laid on the silicon substrate by means of the Langmuir–Blodgett technique. Those spheres act as lenses to focus the laser light. A network of nano-holes (typical diameter: 450 nm) is thus created on the silicon surface. Such a sample is studied by Raman spectroscopy using excitation wavelengths at 488 nm, 514.5 nm and 632.8 nm. For each wavelength, measurements are performed with various laser powers. A clear enhancement of the silicon Raman mode is observed, whatever the excitation wavelength and the laser power are. Our results confirm the possibility offered by such nanostructured samples to highly increase light–silicon interaction.

2. Experimental

Oriented (100) silicon wafers (from Siltronix) are used in the experiments. The wafers are polished on a single side and cut into $\approx 2 \times 2\,cm^2$ area samples. They are sonicated in water and ethanol for 30 min, and further treated with a plasma torch (Acxys technologies) in order to remove any residual contamination and to increase the wettability of the surface.

Afterward, silica spheres with radii of 500 nm and low size dispersion (polydispersity index PDI < 0.2) are mixed with ethanol (40 mg/mL). A Langmuir–Blodgett (LB) film deposition machine (KSV-Nima, model Mini) equipped with a surface tension balance is employed to grow a close-packed sphere monolayer on the Si substrates. We choose to work with C18 functionalized commercial spheres (from Micromod) as they are strongly hydrophobic, enabling the self-assembly of spheres at the air/water interface without the use of chemicals [18,19] that would modify the spheres or the LB subphase. The microsphere solution is carefully spread by small droplets (μL) at the surface of water which is then compressed until the surface pressure reaches 15 mN/m. The monolayer is then transferred to the silicon surface at a dipping speed of 5 mm/min while the surface pressure is maintained at a constant level by progressive automated compression.

The microsphere 2D-arrays obtained on silicon are irradiated by laser pulses provided by an ArF ($\lambda_{laser} = 193$ nm) laser source (from Lambda Physik, LPX220i). The laser pulse duration is 15 ns, and the experiments are performed at normal incidence. The spheres act as near-field focusing elements producing a periodic assembly of sub-diffraction limit light spots (also called photonic nanojets) hitting the silicon surface [20]. When modest laser fluences are used, the substrate is ablated only locally at the tip of the photonic nanojets leaving behind an array of nanocraters in a simple, dry and fast single laser processing step [21].

Obviously the quality of the periodic structuring depends on the quality of the arrangement resulting from the sphere assembly, the level of monodispersity of the spheres and also on the laser dose impinging the substrate [22]. The laser-pulse energy was varied with the aid of a manually operated beam attenuator (from Optec, AT4030).

In previous works [23], parallel and long range ($\gg mm^2$) structuring at the mesoscopic scale (100 nm–1 μm) has been demonstrated on silicon samples showing the interest of this approach. We also studied the degree of control in surface structuring while varying the laser fluence and the number of shots. The results relied on statistical analyses of the created features (in the range 100–1000 nm) observed by optical and scanning electron microscopy (SEM, JEOL JSM-6390) [23]. In the present case, the templates are prepared with 10 laser shots at a laser fluence maintained at 0.55 J/cm^2. This sequence is found to provide

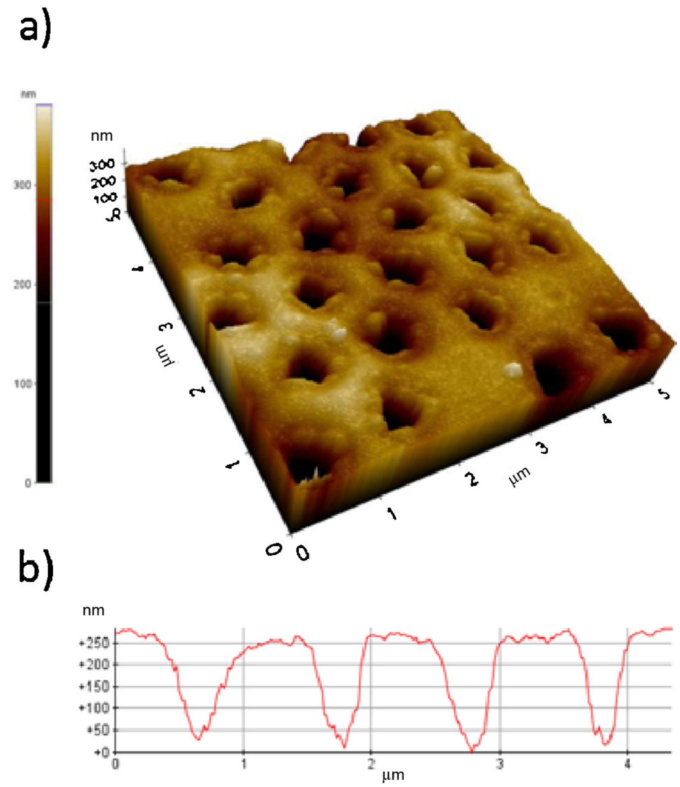

Fig. 1. AFM image of a laser-impacted silicon sample. (a) General 3D view and (b) typical line profile of the nanoholes array.

high quality structures for experiments performed at ambient air. The structures rely on the local ablations induced by the first pulse which ejects the microsphere and leaves a small hole behind it.

Cleaning as well as local ablation of the resulting products around the holes is realized with the following laser pulses. Similar results could be likely obtained with a single laser pulse if the interactions were performed in a low pressure environment to avoid redeposition.

The morphology of the silicon templates used for the optical experiments is analyzed using tapping-mode atomic force microscopy (AFM, PSIA XE-100). An AFM image of the laser-impacted silicon sample can be seen in Fig. 1. A hexagonal network of holes is formed after laser ablation. The pitch is 1 μm imposed by the sphere radius. The holes have a typical diameter of 440 nm and a deepness of 230 nm.

Raman measurements are performed using a Horiba LabRam HR800 spectrometer. Three different laser excitation wavelengths are used: 632.8 nm (from a HeNe laser), 514.5 nm and 488 nm (from an Ar laser). The laser beam is focused on the sample through a $\times 100$ objective (numerical aperture of 0.9). The laser spot size is similar to the typical diameter of the nanoholes. As a consequence, the signal relies on an individual nanohole for each Raman measurement. The use of different laser excitation wavelengths insures a rather broadband study of the optical response of the sample. The laser power varies between 1 μW and 3.6 mW.

3. Results and discussions

For the different laser excitation wavelengths, two kinds of Raman measurements were performed: one with the laser focused on a hole and the other one on a flat part of the sample between the holes. Despite the high power laser irradiation, the Raman signal coming from the flat part of the laser-impacted silicon sample is identical to the one from a standard flat silicon sample (position