Nano and micro-morphology modifications of Si (100) substrate induced by femtosecond laser pulse irradiations in air, water, CCl_4 and $C_2Cl_3F_3$

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The aim of this study is to investigate the influence of the different media, e.g. air, water, CCl_4 (carbon tetrachloride) and $C_2Cl_3F_3$ (tricloro-trifluoro-ethane), when irradiating a Si (100) substrate, with a 200 femtosecond (fs) laser pulses of a Ti:sapphire laser operating at 775 nm. Various micro and nanomorphologies could be achieved by changing the media, the laser pulse energy and the number of pulses. It is shown that the resulting Si (100) surface presents a regulated morphology in air consisting of parallel ripples and the formation of regular arrays of submicrometer spikes on Si (100) in CCl_4 and $C_2Cl_2F_3$, respectively. Irradiation of a Si (100) substrate immersed in water creates a regularly structured surface but it doesn't facilitate the spikes formation. The potential use of the patterned Si substrates as model scaffolds for the systematic exploration of the role of 3D micro/nano morphology on cell adhesion and growth is envisaged.

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1. Introduction

Since femtosecond pulsed lasers have been readily available for laboratory usage, it has been shown that ultra-short pulse lasers have a lot of potential for commercial and laboratory uses in various applications. Strong light excitation irreversibly changes materials for possible new fabrication and micro-/nano-machining techniques. The irradiation of silicon surfaces with femtosecond laser pulses in the presence of some kind of gases transforms the flat, mirror-like surface of the silicon wafer into a forest of microscopic spikes. The microspiked silicon, alternatively called black silicon due to its large optical absorption which causes it to look very black, has potential applications [1, 2]. Successful fabrication of high-density regular arrays of nanometer-scale rods on silicon wafers in liquids (water) with the irradiation of femtosecond laser pulses at a laser wavelength of 800 nm was also communicated [3]. The nanostructures are formed by carving the substrates with a femtosecond laser; the microscopic spikes are in the same body with the substrate and remain with the same lattice structure of the substrate. The spikes/rods formed in a liquid are several orders of magnitude smaller than those formed in gases or in vacuum. This type of structures have different potential applications, such as in biology to make nanomagnetic concentrators to control the growth of cells, or in nanomanufacturing to make master substrates for soft nanolithography to fabricate polymer nanostructured surfaces for sensors at low cost [4]. The mechanism of nanostructure formation under femtosecond laser pulse irradiation is still not well understood. In this paper, we have studied the modifications induced by the femtosecond laser irradiations in four different media: i) air, ii) water, iii) liquid CCl_4 (carbon tetrachloride) and iv) liquid $C_2Cl_3F_3$ (tricloro-trifluoro-ethane) on Si (100) substrate. Decomposition of the previously mentioned liquid substances in thermal plasma atmosphere were studied theoretically [5] and indicates the formation of radicals like CCl_3, CCl_2, Cl_2, CCl_3F_3, F_3. We show that the different media induces a different 3D-design, due to the influence of the radicals containing Cl and F, like in the case of using similar gases [2].

The Si (100) substrate was irradiated with a 200 femtosecond (fs) laser pulses of a Ti:sapphire laser operating at 775 nm. Scanning Electron Microscopy (SEM) was employed to characterize the laser induced single shot area. Variation of the laser fluence and number of pulses caused remarkable changes in the Si structure as to ratio, dimension and density. Changing the media can be used for the control of the height and size of the Si spikes.

2. Experimental

The equipment used to create the micromachining of the Si (100) substrate is a standard laser micro-processing setup in air [6]. The laser source is a commercial

Ti:Sapphire (Clark MRX 2101) regenerative amplifier working in chirped pulse amplification (CPA) configuration. The laser delivers pulses with 200 fs duration, at 775 nm wavelength and 2 kHz repetition rate [7]. The laser beam (Gaussian beam shape) was focused onto the surface by a 75 mm convex lens with BestForm shape, corrected for reduced spherical aberrations (estimated spot diameter 26 µm). The samples are precisely translated and positioned by a XYZ computer controlled translation stage, equipped with stepper motors which provide displacement accuracy in the range of few hundreds of nanometers with a translation speed covering the domain between 5 µm/s and 1 mm/s (Fig. 1a). The processed surface is monitored in real-time by a monochrome CCD camera with a 200 mm tube lens. The optical resolution is below 1 µm.

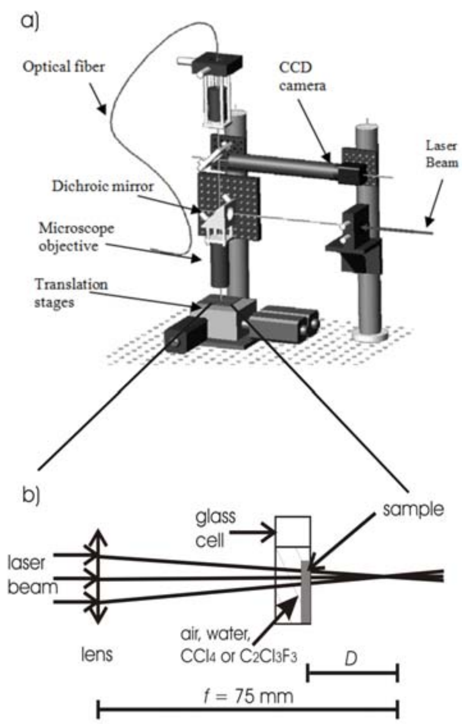


Fig. 1. Schematical representation of experimental setup: a) a standard laser micro-processing setup in air, b) the optical path in the experiments, f is the focal length and D is the distance between the sample and the focal point.

The laser pulses are continuously controlled in the range of a few nJ up to hundreds nJ by a variable attenuator composed by a half waveplate and a Glan-laser polarizer. The laser energy is measured in the front of an attenuation system by a laser energy meter and corrected by the optical transmission of the lens/microscope objective. The irradiating energy was altered by neutral attenuators. We place Si (100) (purchased from Crystal GmbH) in a glass container filled with: i) air, ii) de-ionized water (TKA Pacific UP/UPW6), iii) CCl_4 and iv) $C_2Cl_3F_3$ and scanned the sample by the femtosecond laser at normal incidence (Figure 1b). We have performed cleaning procedures in order to change the hydrophobic Si (100) substrate into a hydrophilic Si (100) substrate. The Si substrates were first treated with a solution of H_2O_2 (30% - 40% conc.), NH_3 (25% conc.) and H_2O volume ratio 1:1:5. This procedure was followed by a thermal heating of the substrate at 80 °C for 10-15 min. For the second step, a mixture of H_2O_2 (30% - 40% conc.), HCl (25% conc.) and H_2O volume ratio 1:1:6 was used. The Si substrate was again heated at 80 °C for 5-10 min. The Si surface was in such a way oxidized and charged negatively, with an easily observable hydrophilic characteristic. The hydrophilic behavior is similar with the similar characteristic obtained using the CCl_4 and $C_2Cl_3F_3$ liquids. After laser irradiation, the samples are investigated by SEM.

3. Results and discussions

1) Determination of the single-shot ablation threshold for Si substrate

A frequently used technique for determining the ablation threshold was developed by Liu to measure the diameter of a Gaussian laser beam by examining the ablation diameters on a material surface at various laser energies [8]. The dependence of the ablation spot size on the ablation threshold fluence and peak incident laser fluence for a Gaussian profile beam is given by:

$$d^2 = 2w_0^2 \ln\left(\frac{F_{las}^{peak}}{F_{th}}\right) \tag{1}$$

where d is the diameter of the ablation spot, w_0 is the e-folding electric field amplitude beam radius for a Gaussian beam spot, F_{las}^{peak} is the laser peak energy density (fluence) and F_{th} is the ablation threshold fluence, that is the minimum laser fluence (laser energy per unit surface) required for ablation. For a pulsed Gaussian beam F_{las}^{peak} is given by:

$$F_{las}^{peak} = \frac{2E}{\pi w_0^2} \tag{2}$$

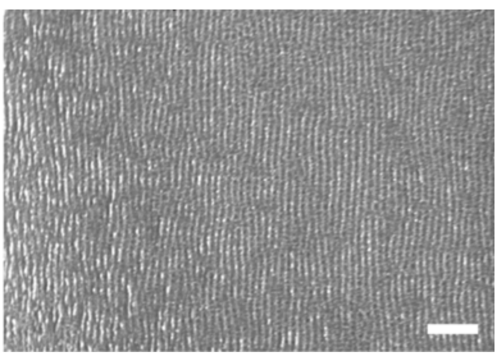
where E is the energy per pulse, which can usually be measured by inserting an energy meter into the raw beam, and w_0 is the $1/e^2$ radius of the beam in the plane normal to the direction of propagation. For a perfect Gaussian beam the spot radius, w_0, can be calculated from the laser wavelength λ, the focal length of the lens *f*, and the radius of the beam before the lens w_1, using the equation:

$$w = \frac{\lambda f}{\pi w_1} \tag{3}$$

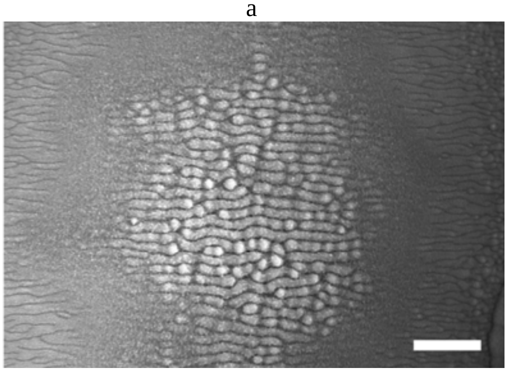
Since no beams are perfect the deviation from a purely fundamental TEM00 mode structure is normally accounted for by substituting $M^2\lambda$ for λ, where M^2 is the beam quality factor (in our case M^2 is 1.5 and $w_1 = 2$ mm).

The ablation threshold for the Si substrate was measured for a single-shot ablation. The laser spot was focused with a convex lens with f = 75 mm, resulting w = 13 µm. We found that the threshold fluence for damage of silicon in air is 0.28 J/cm^2, which is in agreement with the literature results [9]. When we change the distance between the substrate and the focal point, D (as shown in Fig. 1b), the laser spot size (the 1/e^2 width) can vary from about 28 µm to 534 µm. In the experiment, we first use a silicon substrate when the cell is filled with air to find the location where a silicon substrate just starts to become damaged, and the fluence at this location is 0.28 J/cm^2, as previously mentioned. Then the fluence at other locations can be calculated by the assumption that the laser beam is composed of parallel light rays before the lens (see Fig. 1b). In our case, we choose a fixed D, giving a focus spot diameter of 428 µm and vary the fluence range by using a series of variable neutral attenuators.

i) When the media is air, in the Fig. 2 we present a SEM image of the single shot irradiation area for F_{las}^{peak} = 0.5 J/cm^2 and 50 pulses, in the periphery (a) and F_{las}^{peak} = 0.5 J/cm^2 and 500 pulses, in the central zone (b).



a

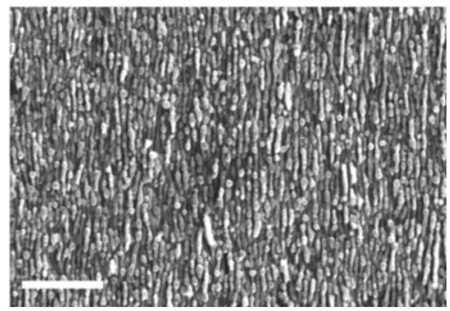


b

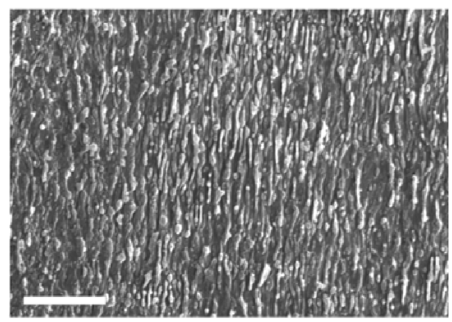
Fig. 2. SEM image of the Si (100) substrate after irradiation with Ti:Sapphire laser pulses in air (F_{las}^{peak} = 0.5 J/cm^2, 50 pulses) of the periphery area indicating the formation of vertical ripples with scale bar 2 µm (a) and of the central area indicating the formation of horizontal ripples with scale bar 4 µm (F_{las}^{peak} = 0.5 J/cm^2, 500 pulses) (b).

These images are representative for the evolution of the Si substrate morphology in air under the irradiation with different number of fs laser pulses at the same fluence. The periphery area shows regulated structure of vertical ripples with 300 nm periodicity (Fig. 2a), while the central area develops horizontal ripples formation by increasing the number of the laser pulses to 500 at the same fluence. In these conditions, we obtain a larger periodicity of the ripples of 2.4 µm (Fig. 2b).

ii) When the media is water, the SEM investigations showed in the Fig. 3a) and b) put into evidence a different behavior. For the whole irradiated zone, the SEM measurements put into evidence regular structure of ripples, with a higher density (in the central zone, Fig. 3a) and lower density (at the periphery zone, Fig. 3b).



a



b

Fig. 3. SEM image of the central zone of a Si (100) substrate after irradiation with 500 laser pulses, F_{las}^{peak} = 0.39 J/cm^2 in water (a); scale bar 2 µm, SEM image of the periphery area indicating the formation of vertical ripples (b) scale bar 2 µm.

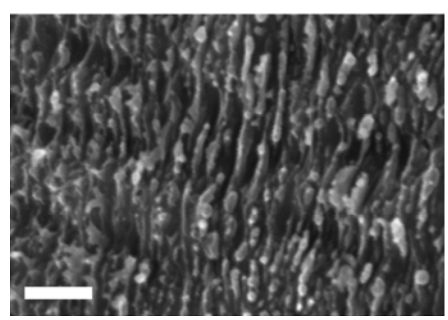
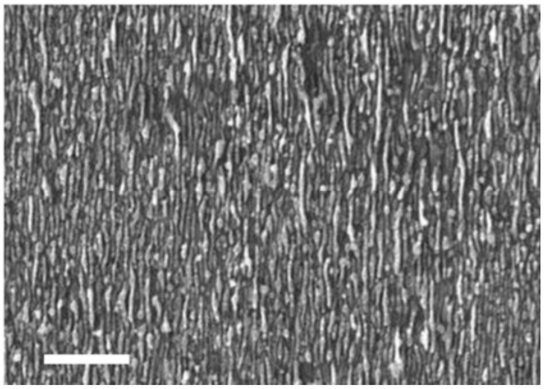
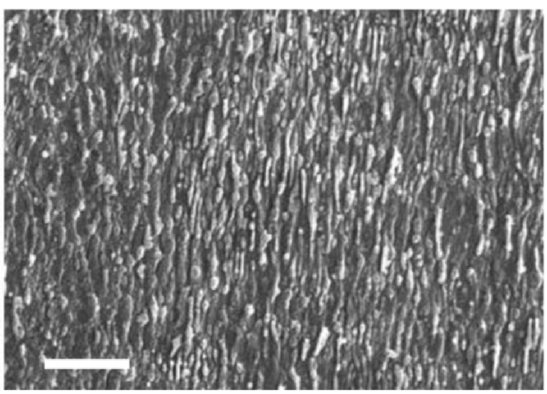


Fig. 4. SEM angle view image of the Si (100) substrate after irradiation with a 200 fs laser, λ= 775 nm, F_{las}^{peak} = 0.39 J/cm^2, 500 pulses in water scale bar 1 µm.

Fig. 4 represents a SEM picture viewed at an angle of 30º from the surface normal. The image indicates, along with the ripple formation, a process of etching that takes place during the laser irradiation in water. The structures gain a depth profile in the Si (100) substrate.



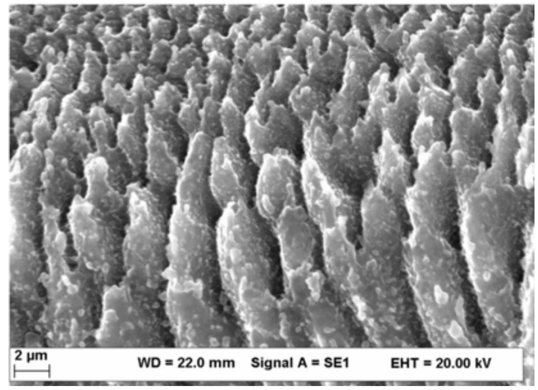
a



b

Fig. 5. SEM images of ripples structure in (a) hydrophilic and (b) hydrophobic silicon surface irradiated with Ti:Sapphire laser pulses in water (F_{las}^{peak} =0.39 J/cm^2, 500 pulses).

We made the comparison between the results obtained by irradiating a hydrophilic Si (100) surface and a hydrophobic Si (100) one. The SEM results are represented in the Fig. 5a) (the case of a hydrophilic Si) and Fig. 5b) (the case of hydrophobic Si). The images put into evidence a different ripples periodicity from a case to another at the nanometric scale.



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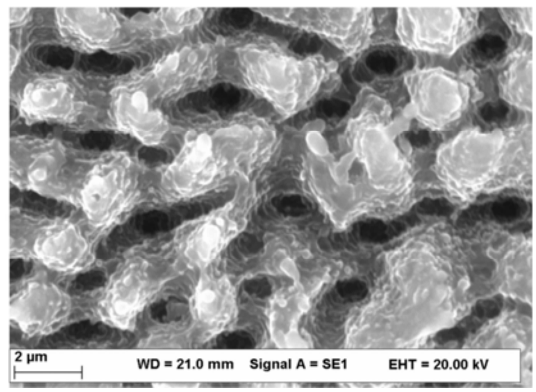

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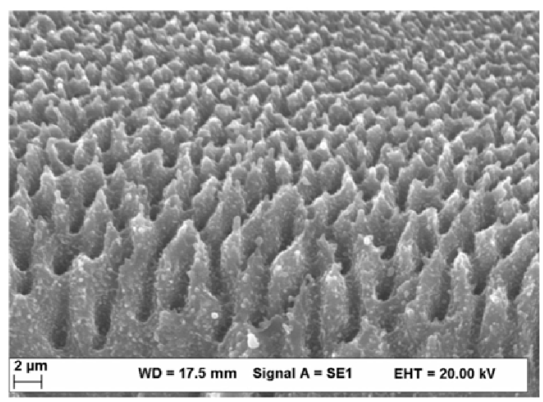
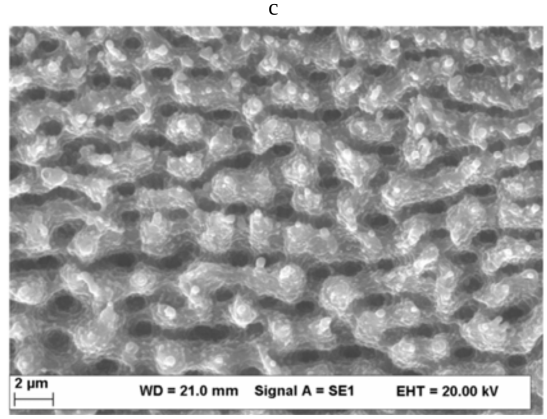


c



d

Fig. 6. SEM micrographs of silicon spikes formed in CCl_4 (a), (b) and $C_2Cl_3F_3$ (c), (d) (F_{las}^{peak} =0.56 J/cm^2, 700 laser pulses).

iii) Another medium of investigations was CCl_4 and the results are shown in Fig. 6 a) and (b). Here we can observe the rough spikes produced in CCl_4 at F_{las}^{peak} = 0.56 J/cm^2 and 700 laser pulses viewed at an angle of 30º from the surface normal (a) and top viewed (b). The spikes which are uniformly distributed in periodically arrays are up to 4 µm tall and have a full width at half maximum of 2.3 µm.

iv) As a comparison, it can be seen in Fig. 6(c) the sub-micrometer spikes obtained by irradiating the silicon surface immersed in $C_2Cl_3F_3$ at a lower fluence and less laser pulses than in the previous case (F_{las}^{peak} = 0.33 J/cm^2, 400 pulses). Here the average height of the spikes is 4.2 µm and the full width at half maximum is 890 nm (three times smaller than those obtained in CCl_4).

As we can observe in Fig. 6(b), the etching spot diameter (in the SEM image represented by the dark spots) in CCl_4 is about 710 nm which is smaller than the one obtained in $C_2Cl_3F_3$ (850 nm, Fig. 6(d)). We attribute these differences to the influence of the F radicals that give a smaller etch diameter in comparison with the Cl radicals.

By irradiating the Si sample immersed in CCl_4, beyond the region which presents spikes, we observed the appearance of the ripples configuration. Here the periodicity of the ripples is 370 nm µm smaller than the one obtain in air and water at the same parameters (Fig. 7).

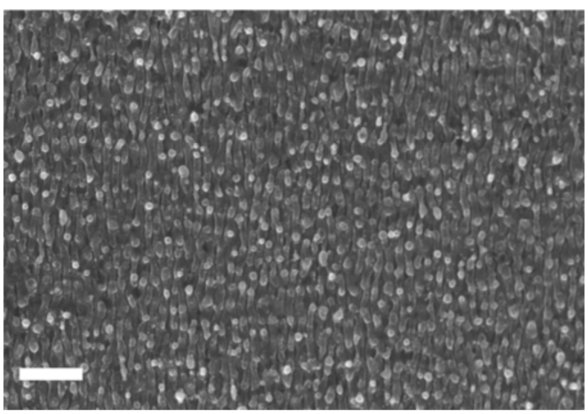


Fig. 7. SEM image of ripples structure of the Si (100) substrate after irradiation with Ti:sapphire laser pulses (F_{las}^{peak} = 0.56 J/cm^2, 500 pulses) in CCl_4 (a) scale bar 2 µm.

Such periodic ripples with spacing about few hundreds nanometer were observed by other authors which produced these structures on various highly absorbing polymers [10] or in same conditions on silicon surface, in air or water [11].

4. Conclusions

We have obtained the formation of sub-micrometer spikes on a silicon surface irradiated by a series of variable fluence femtosecond laser pulses in CCl_4 or $C_2Cl_3F_3$ and the ripples structure in presence of water or air. The difference between the spikes dimensions obtained in both cases is due to the etching process which occurs in CCl_4 and $C_2Cl_3F_3$. The influence of the radicals, Cl or F, is observed in the SEM investigation. The presence of the F radical makes the etching process more uniform on a larger scale. The etching spot diameter in CCl_4 is about 710 nm, smaller than the one obtained in $C_2Cl_3F_3$ which is 850 nm. The average height of the spikes for the case of $C_2Cl_3F_3$ is 4.2 µm and the full width at half maximum is 890 nm, while for the case of CCl_4 these are 4 µm and 2.3 µm, respectively.

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