Morphology of IR and UV Laser-induced Structural Changes on Silicon Surfaces.


Abstract. Using scanning electronic microscopy, we analyze the structural changes induced in silicon (100) wafers by focused IR (1064 nm) and UV (355 nm) nanosecond laser pulses. The experiments were performed in the laser ablation regime. When a silicon surface is irradiated by laser pulses in an O₂ atmosphere conical microstructures are obtained. The changes in silicon surface morphology depend both on the incident radiation wavelength and the environmental atmosphere. We have patterned Si surfaces with a single focused laser spot and, in doing the experiments with IR or UV this reveals significant differences in the initial surface cracking and pattern formation, however the final result consist of an array of microcones when the experiment is carried out in oxygen. We employ a random scanning technique to irradiate silicon surfaces over large areas. In this form we have obtained large patterned areas.

INTRODUCTION

When high intensity laser radiation is absorbed by a solid surface, the electromagnetic energy is converted first into electronic excitation and then into thermal, chemical, and even mechanical energy which causes evaporation, plasma formation, and exfoliation. Evaporants form a “plume” consisting of a mixture of energetic species including atoms, molecules, electrons, ions, clusters, micron-sized solid particles, and molten globules [1].

Laser pulses rarely remove material in a clean, orderly, layer-by-layer fashion. Instead, laser-irradiated surfaces become altered both physically and chemically. Morphological changes may take the form of periodic structures such as ripples, ridges, and the most intriguing features of all, cones [2].

Conical structures have been observed in metals, ceramics, polymers, and semiconductors as a result of repetitive pulsed-laser irradiation, at laser fluences in the range of 1.0 to 10.0 J cm⁻² (ablation regime) [2].

More recently using fs infrared pulses and very reactive atmospheres (SF₆ or Cl₂) very sharp conical structures have been obtained [3].

In this paper we report the growth of the conical structures on the surface of silicon (100) upon cumulative pulsed-laser irradiation both at the Nd:YAG fundamental (1064 nm) and third harmonic (355 nm) wavelengths in presence of an oxygen atmosphere. Additionally to irradiate samples by focusing the laser beam on a fixed
point of the target, we employ a random scanning technique to irradiate silicon surfaces over large areas. In order to verify the role of the atmosphere in this photoetching process, we also irradiate silicon wafers in vacuum. We show the differences between these laser-etching processes at its initial stages and also once the microstructures have became fully growth under both IR and UV irradiation.

**EXPERIMENTAL SETUP**

We carried out our experiments on n-type (arsenic-doped) Si (100) wafers with resistivity less than $7 \times 10^{-5}$ $\Omega$ m. The samples are ultrasonically rinsed in methanol in the first place, then in acetone and finally in 5% HF(aq) solution. The wafer is mounted in a vacuum chamber with a base pressure of less than $10^{-5}$ Torr. The chamber is backfilled with (normally) 100-Torr of O$_2$.

The laser used for irradiation is a Nd:YAG (Lumonics HY1200) with a maximum output of 1.2 J per pulse at 10 Hz repetition rate in the fundamental wavelength (1064 nm) and 10 ns pulse width, all the samples have been irradiated at normal incidence. The laser beam is focused with a quartz lens in order to obtain the desired energy density ($\approx 6$ J cm$^{-2}$).

We use a random scanning technique to irradiate silicon surfaces over large areas. In this technique the laser beam is reflected by two computer-controlled mirrors such that we can guide the beam at will.

![Experimental setup diagram](image)

**FIGURE 1.** Experimental setup. A Q-switched Nd:YAG laser generating up to 1.2 Joules at 1064 nm and the 2$^{\text{nd}}$, 3$^{\text{rd}}$ and 4$^{\text{th}}$ harmonics is used to irradiate Si samples in a HV chamber with base pressures down to $10^{-5}$ torr. For the experiments reported here, we have used the fundamental and the 3$^{\text{rd}}$ harmonic of the system.

For this scanning technique, we define the area we wish to irradiate and with the help of the computer controlled mirrors we irradiate the sample within the designed
region such that, on average, we apply the same dose per unit area that we would apply to a single laser spot, i.e without steering the beam every shot.

EXPERIMENTS

IR (1064 nm) pulsed-laser irradiation in O₂

After the first 60 laser shots, fractures begin to develop on the irradiated surface under an oxygen atmosphere. As show in Fig. 2a and Fig. 2b, for (100)-oriented wafers, two sets of fracture lines intersect at 90° forming a grid that divides the surface into rectangular blocks. Furthermore, the images reflect the variation of the fluence across the laser spatial profile.

The fractures open up with increasing number of laser pulses, and deep grooves and craters develop from these fractures. The rectangular blocks in which the original surface is split will form the base of the microcones and –we believe-, the material expelled from the grooves will form the cones.

In Fig. 2c and Fig. 2d we can see the conical microstructures produced after 2000 laser shots viewed at an angle of 45° from the surface normal. The growing direction of the cones always coincides with the direction of the incident light.

On the other hand, we have patterned larger areas (≈100 mm²) by randomly scanning the laser beam across the sample such that each point within the selected region receives the same dose. The resulting structure is showed in Fig. 3. In all our experiments both energy density and oxygen pressure remained fixed. Using the method just described we obtain also cones (see figure 3d), although not as sharp as the ones showed in figure 2d, when the irradiation is performed in a single point.

When we have patterned areas larger than the laser spot, we have observed similar behaviour, first the cracking of the surface, then deep grooves forming from the cracks and finally the growing of the conical structures that protrude above the original surface.
UV (355 nm) pulsed-laser irradiation in O₂

Following the same sequence, in Fig. 4a and Fig. 4b we can see the superficial morphology at the first stages, in which we found that irradiated surface is not conformed by rectangular blocks, but by structures what appear to be capillary waves.

After irradiation of the sample with 2000 pulses, the surface shows several regions, but only one of them shows the conical structures, as it is shown in Figure 4c.

When we performed random irradiation with 1000 pulses the silicon surface increases its roughness, however we have not found fractures. After 30000 pulses, fractures begin to develop on the irradiated surface similar to first stages of IR-laser irradiated surface.

In order to verify the importance of the atmosphere in these experiments we performed random irradiation in vacuum with IR laser (1064 nm). After 50000 pulses, almost all the surface shows what appears to be capillary waves. However there are zones in which we can see some protruded rounded holes and deep grooves (Fig. 5a). Increasing the number of shots (100000), the entire surface becomes covered with microcones (Fig. 4b). The difference between the vacuum microstructured surface...
and the one reactive atmosphere (oxygen) consists in the lack of the initial craking of the surface and as a consequence of this a more random distribution of the cone’s position, compare, for example Fig. 5b and Fig. 3b.

**FIGURE 5.** SEM images (normal incidence, except (c) and (d) of a Si(100) specimen randomly irradiated (=100 mm²) at a laser fluence of 6 J cm⁻² with IR pulses in vacuum (i.e. P~10⁻⁵ Torr) (a) early stages (50000 laser pulses), (b) after 100000 laser shots, (c) and (d) higher magnification viewed at an angle of 45⁰ from the surface normal.

**Discussion.**

**Experiment at 1064 nm.** Fractures similar to the ones observed in Fig. 2a and Fig. 2b were already reported by Lowndes et. al [4] they found them after irradiate a Si(001) surface with KrF excimer laser (248 nm, 25 ns). In our case, these fractures form a pattern which follows the symmetry of the Si wafer, i.e., lines intercepting at 90 degrees for Si(100). In this process, the structures formed on the surfaces show a characteristic period that is smaller than the spot size of the laser and larger than the wavelength of the radiation used [5].

Despite previous results [6] where excimer laser irradiation produced microcolumn patterns, in this work we report that a conical microstructure array is always obtained when the sample is irradiated by IR laser pulses at 1064 nm in presence of O₂. Whilst irradiating in vacuum, we obtained mountain-like structures and not the sharp conical structures we can see in figure 1d, the growing of these structures is much slower compared when we have an O₂ atmosphere, so the role of the etching gas is very relevant for both, the growing of the microstructures and their shape.

**Experiment in O₂ at 355 nm.** The Si(100) surface morphology irradiated with more energetic photons (355 nm) presents significant differences in respect to surface irradiated with IR-photons (1064 nm). The structures what appear to be capillar waves had been previously reported when the experiment carried out with a copper vapour laser (wavelength of 510.6 nm, pulse duration of 20 ns) [7].

In conclusion, when a Si wafer is irradiated with a high power Nd:YAG laser either in λ=1064 nm or λ=355 nm the morphology of the surface changes, these changes begin with cracks on the surface, capillary waves and finally micron-sized structures, being these sharp conical structures (with O₂ and IR light) or mountain-like structures (with UV light or IR in vacuum). This points towards that the mechanism of growing
is likely to be different depending on the wavelength of the irradiation and the ambient atmosphere. Currently, we are further investigating these processes.

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REFERENCES