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Pulsed TEA CO_2 laser surface modifications of silicon

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Abstract

The interaction of a transversely excited atmospheric (TEA) CO_2 laser, pulse duration of about 2 μs (FWHM of initial spike = 120 ns), with p-type single crystalline silicon doped by boron, was studied. The results have shown that the silicon was surface modified by the laser beam of 12.0 J cm^{-2} energy density. The energy absorbed from the CO_2 laser beam is converted partially into thermal energy, which generates a series of effects such as melting, vaporisation of molten material, shock waves, etc. Morphological manifestations on the silicon surface are: nonuniform modifications (central zone of interaction); wave-like periodical microstructure (inner periphery zone); hydrodynamical structure-like droplets (outer periphery zone). Wave-like microstructure consists of periodic parallel fringes with a period of about 0.8 μm. Formation of these wave-like microstructures is very complex. Explanation includes a consideration of the laser-induced periodic surface structure (LIPSS) effect. The process of the CO_2 laser interaction with silicon was not initially accompanied by plasma. Plasma, in the form of a spark, typically appeared after about 100 cumulated laser pulses.

Keywords: Laser surface modification; Silicon; Laser-induced periodic microstructure; Pulsed TEA carbon dioxide laser

1. Introduction

Surface modification studies of semiconductor materials, including silicon, by various types of energetic beams, including the laser beam, are of a great fundamental and technological interest. Silicon exhibits very good physico-chemical characteristics: high melting/boiling point; thermodynamic and chemical stability; semi-conducting properties, etc. [1]. For these reasons it is very attractive in electronics (industry of semi-conductors), glass industry, as well as an alloying element (in manufacturing, e.g. ferrosilicon alloy), etc. The interest in studies of laser beam interaction with silicon is still high. The Nd:YAG [2,3], excimer [4,5] and CO_2 laser (cw regime) [6] are typically used laser beams for these purposes.

The interaction of a pulsed CO_2 laser beam, with silicon is insufficiently known in literature [7–10]. In the present paper the effects of a pulsed transversely excited atmospheric (TEA) CO_2 laser, which emits infrared radiation at about 10 μm, on the p-type single crystalline silicon doped by boron, were studied. Attention was paid to morphology surface observation, especially to the appearance of periodical microstructures.

2. Experimental

The sample was a boron doped p-type single crystalline silicon with (1 0 0) orientation, in plate form.

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The dopant concentration was below 0.1 at.%. The silicon was of metallic-greyish colour [1]. The dimensions of a rectangular shaped sample were ca. 15 mm × 10 mm × 0.5 mm (length × width × thickness). The standard procedure was applied for preparing the silicon surface prior to the laser irradiation process, which included cleaning, electro-chemical polishing, rinsing and drying. Only the face of the sample was polished, while the backside remained rough.

Sample irradiation was performed with a focused laser beam. A KBr lens with a focal length of 6.0 cm ensured focusing onto the silicon target. The incidence angle of the laser beam with respect to the surface was 90°. The irradiation was carried out in air, at a pressure of 1013 mbar and relative humidity of 60%.

The irradiation source was a TEA CO_2 laser beam. The laser operated with a nontypical $CO_2/N_2/H_2$ mixture [11,12]. The mixture with nitrogen generated a pulse with a tail. Hydrogen typically improves plasma stability within the laser and enhances the output energy [11]. The beam cross-section was multi-mode, near to the quadratic form, so that certain spatial-uniform distribution of the intensity could be assumed [13]. Detailed characteristics of the laser used in the experiment are presented in Table 1.

Various analytical techniques were used for characterisation of the sample. The single crystalline silicone orientation was confirmed by an X-ray diffractometer (XRD). The surface morphology was monitored by optical microscopy (OM) and by a scanning electron microscope (SEM) with secondary (SE) and back-scattered electron (BSE) detectors. A quantitative standardless compositional analysis was carried out by an energy dispersive analyzer (EDAX).

Table 1
Typical experimental conditions for used TEA CO_2 laser

Gas mixture	$CO_2/N_2/H_2$
Content	1/1/1.5
Output pulse energy	To 150 mJ
FWHM[a]	~120 ns (initial spike)
Mode structure[b]	Multi-mode output
Beam divergence[c]	~10 mrad
Laser cavity	Nondispersive
Spectral composition[d]	Simultaneous two-lines operation in P-branch 00°1 → 10°0 vibrational band
Pulse rate repetition	2 Hz

[a] Full width at a half maximum. The laser pulse for $CO_2/N_2/H_2$ mixture, contents initial spike and tail. The tail duration is about 2 μs.

[b] The laser possesses a highly multi-mode output. The unfocused laser beam has near quadratic cross-section with dimensions of about 1 cm × 1 cm.

[c] This value is measured in the relation to near-field.

[d] The laser simultaneously operates at two wavelengths, i.e. 10.5709 and 10.5909 μm, P(18) and P(20) transitions.

3. Results and discussion

The X-ray diffraction analysis of the sample showed that the single crystalline silicon used here was of (1 0 0) orientation.

Laser-induced morphological silicon surface changes showed dependence on beam characteristics, primarily on the laser pulse energy and peak power density. The energy absorbed from the beam is converted into thermal energy, which generates a series of effects such as melting, vaporisation of the molten material, dissociation or ionisation of the vaporised material and shock waves in the vapour and in the solid.

Surface changes in the irradiated zone, registered after 340 and 500 pulses, were more prominent than in with 20 pulses. The morphological features of the silicon for 340 cumulated laser pulses are presented in Fig. 1. The action of the laser radiation under these conditions when the energy deposited was $12.0\ \mathrm{J\,cm^{-2}}$, causes significant surface modification of the silicon surface. It is well known [7,8,10] that silicon is a poor absorber, being basically transparent for CO_2 laser radiation. Modifications were obtained in spite of this. Several mechanisms can be responsible for the absorption of CO_2 laser radiation they are: (i) some absorption due to the presence a lattice phonon [8,14]; the corresponding absorption coefficient is estimated at $1.2\ \mathrm{cm^{-1}}$ at a wavelength of 10.6 μm [8,14], (ii) the presence of free carriers in silicon [7,8,10]. The latter strongly depends on temperature and presence of impurities [8,10]. Accordingly, silicon absorbance changes during the laser irradiation process. Boron was employed as an impurity in our sample. Finally, (iii) presence of defects on the surface or in the bulk. In order to enhance the absorption of the sample, boron doped silicon, i.e. to enhance free concentration of carries, Wang et al. [10] applied an efficient and attractive technique: coating the backside of the specimen with gold or paint.

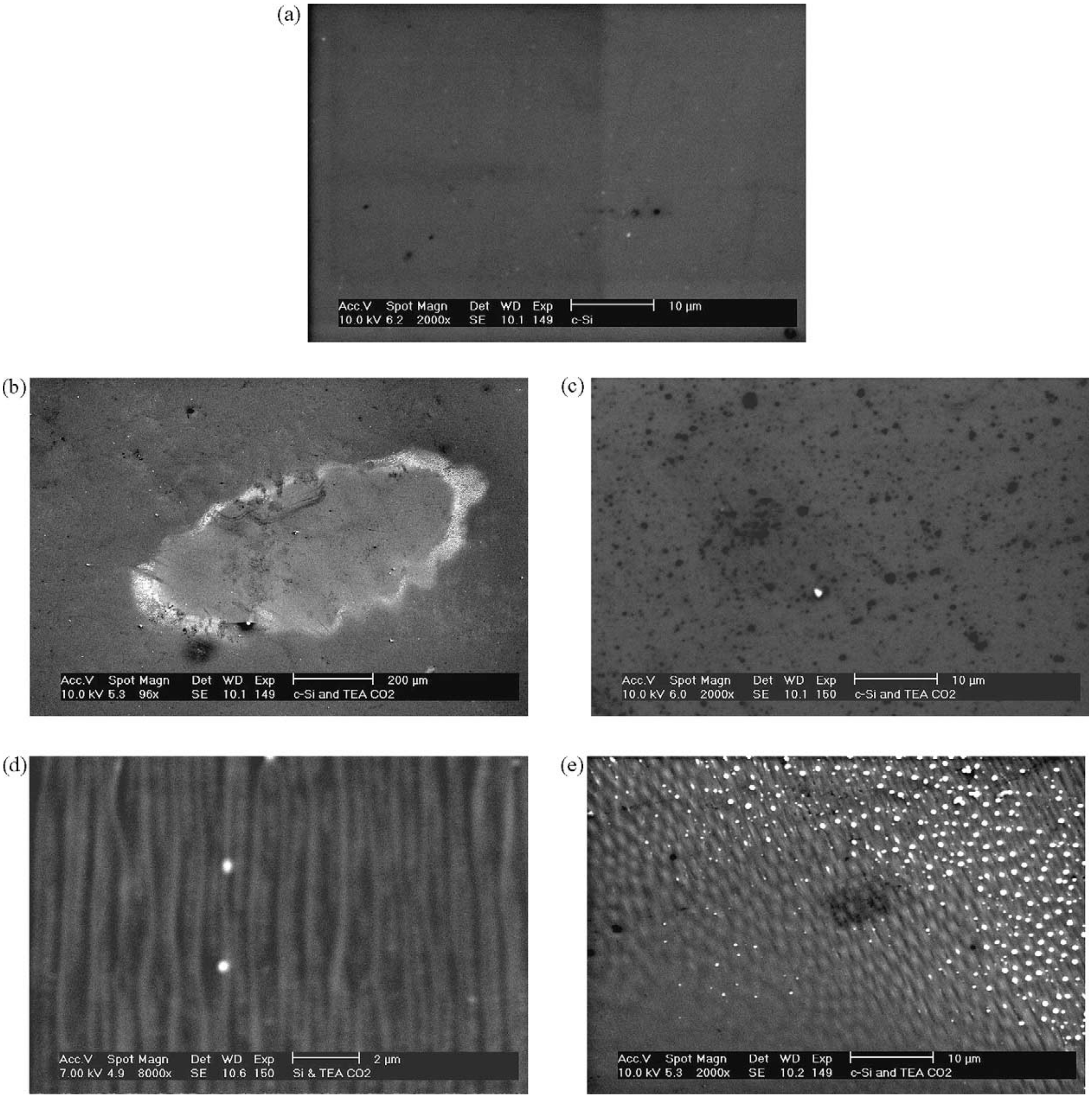

Fig. 1. The morphology of the p-type single crystalline silicon doped with boron induced by TEA CO_2 laser. The analysis has been conducted by SEM. (a) Silicon before the laser treatment. Changes induced with 340 pulses: (b) the entire irradiated area; (c) the central zone; (d) inner periphery; (e) outer periphery of interaction (action of pulse with tail; deposited energy density = 12.0 J cm^{-2}).

In the interaction area, Fig. 1b, nearly three zones can be distinguished: the central zone; inner periphery; outer periphery. In the central zone, Fig. 1c, nonuniform modifications are visible, caused by thermal effects. Wave-like periodical and hydrodynamical structure in the form of resolidified droplets of material were registered in the inner and outer periphery zones in, Figs. 1d and e, respectively. The wave-like structure, i.e. the appearance of periodic fringes on silicon in the course of the experiments was initially

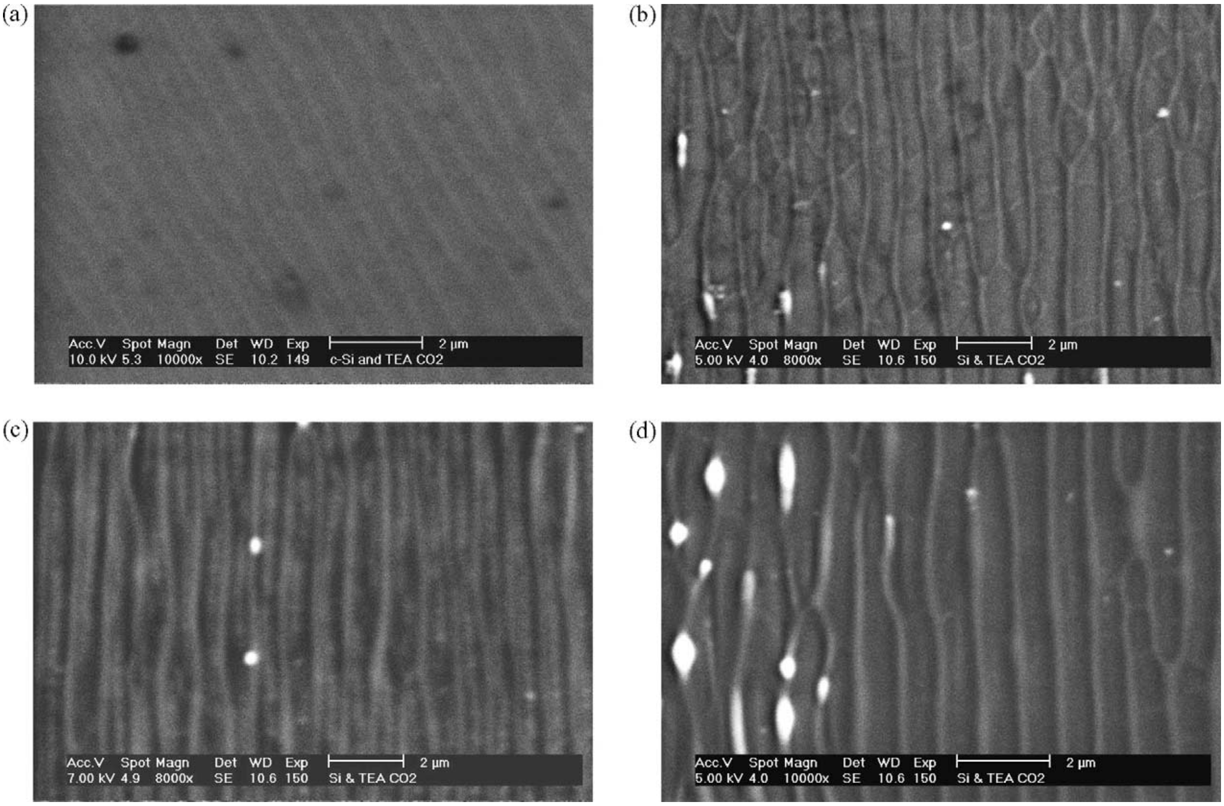

Fig. 2. The morphology evolution of the single crystalline silicon doped by boron, in the inner periphery zone, with number of CO_2 laser pulses. SEM analysis was used. Action of (a) 20, (b) 120, (c) 340, and (d) 500 cumulative laser pulses (action of pulse with tail; deposited energy density $= 12.0\ \mathrm{J\ cm^{-2}}$).

mentioned in [9]. This phenomenon was studied also in [10].

At the beginning, the process of laser interaction with silicon was not accompanied by plasma appearance in front of the target. Plasma, in the form of sparks, was created typically after 100 cumulated laser pulses.

The morphological evolution of the silicon surface in the inner periphery zone with accumulating pulses is presented in Fig. 2. Periodic microstructures were registered in all cases, Figs. 2a–d. Microstructures are clearest after 500 laser pulses. This structure consist of numerous parallel fringes of an estimated width about 0.8 µm. Wang et al. [10] have obtained the width of about 2 µm with the same type of sample and same wavelength. Disagreement of the fringe widths measured in our experiment with those of Wang is very intricate for consideration. Creation of micro-structures (MS) with a period close/different than the laser wavelength used is known in literature [4,15,16]. It should be pointed out that in both experiments all conditions were quite different, e.g. laser pulse lengths, beam polarisation, characteristics of the sample backside, etc. except for the laser wavelength. Laser beam properties, like polarisation and coherence, as well as the angle of incidence to the target, can affect the spatially periodic energy deposition, including the appearance of MS [15,17]. Wang et al. [10] also report that the size of MS, including the fringe width, can be controlled precisely by controlling laser parameters. In the light of these facts, the difference in experimental conditions is probably most responsible for the variation of the fringe widths.

Generally speaking, the explanation for formation of MS is very complex [4,10,15]. Basically, fine microstructures are produced by the laser-induced periodic surface structure (LIPSS) effect [10,15,17–19].

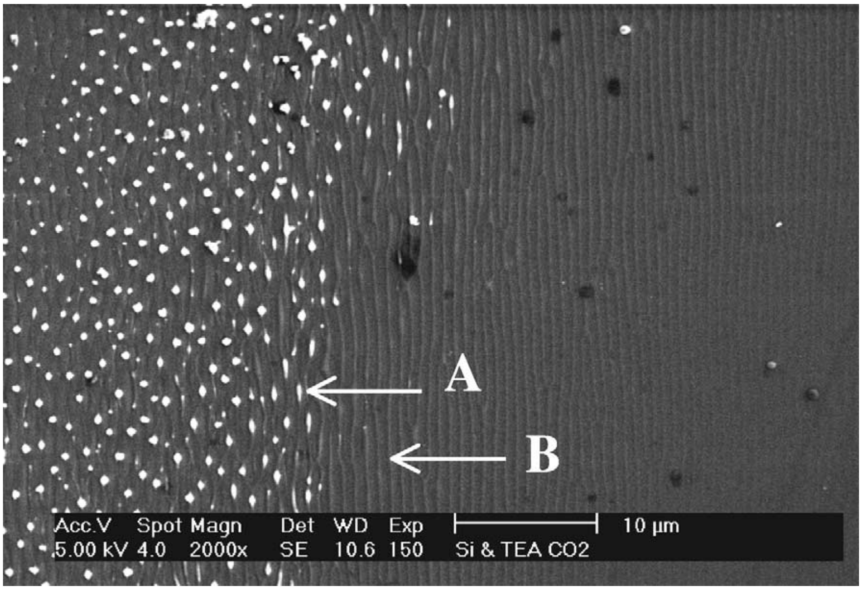

Fig. 3. The morphology features, of the single crystalline silicon doped with boron, in the inner periphery zone after action of 500 CO_2 laser pulses. SEM analysis was employed. The irradiation conditions were the same as in Figs. 1 and 2. Marks A and B are the locations for EDAX analysis, (A) denotes the top of the droplet, and (B) the fringe of the microstructure.

LIPSS is a universal phenomenon which includes semiconductors, metals, etc. and appears on any material that absorbs laser radiation [15,17,19]. The LIPSS effect [15,17,18] includes: (i) area of low laser energy density action on the target, with spatially periodic melting induced by inhomogeneous energy deposition on a solid target; (ii) area of high laser energy density action, with induced capillary waves on a completely liquid surface [15]. In these regimes the cross-sectional contour of the ripples can vary significantly. The spatial period of the ripples, in some manner, is a function of the laser energy density used [15]. The spacing is defined by radiation residues produced at the solid/air interface or by the surface plasmon stimulated at the liquid/air interface for low and high laser energy density, respectively, [15]. Also, the role of intra- and inter-pulse feedback can be included in this consideration.

After 120 pulses hydrodynamic effects, solidified droplets on the surface, are recorded simultaneously with periodic microstructures, Fig. 2b. This effect is particularly expressed after 500 laser pulses, Figs. 2d and 3.

It can be assumed that chemical changes, like oxidation, etc. occur on the silicon surface during the irradiation. In this context quantitative standardless compositional analysis of the sample, before and after laser irradiation, was performed with EDAX, Figs. 4a and b, Table 2. Before laser action, Fig. 4a, the surface concentration of oxygen was found to be 0.8 at.% in silicon. After laser action, Fig. 4b, oxygen concentration was about 6.0 at.%. The analysis after the laser irradiation was carried out at two locations, A and B, Fig. 3, i.e. at the centre and outside the droplet boundaries. In both the locations oxygen concentration was similar, i.e. about 6.0 at.%.

As the irradiation of the silicon was performed in air, and the enhancement of oxygen concentration

Table 2
Analysis of elements on the silicon surface by EDAX

Element	Before laser action (at.%)[a]	After laser action[b] (at.%)
Oxygen[c]	0.8	6.0
Silicon[c]	99.2	94.0

[a] The unit at.% denotes the element concentration in percent.
[b] Analysis was performed at two locations as shown in Fig. 3.
[c] Kα emission lines of each element were used for its analysis. Boron concentration (<0.1 at.%) was below the sensitivity of the instrument.

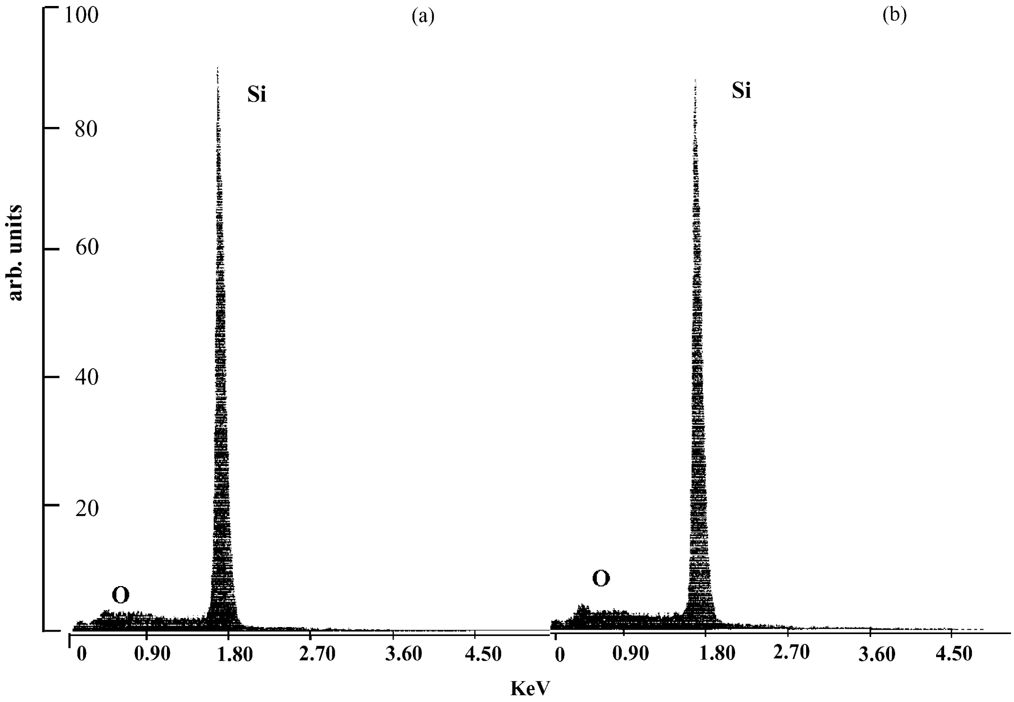

Fig. 4. EDAX analysis of silicon: (a) before and (b) after laser action. About 500 cumulative laser pulses were applied on silicon; pulse laser energy density was the same as in Figs. 1 and 2.

upon laser action was obtained, the most probable effect that occurred was partial oxidation of the silicon surface.

4. Conclusion

A qualitative consideration of the morphological changes on silicon surface induced by pulsed TEA CO_2 laser is presented. It is shown, here and in [9], that a TEA CO_2 laser can induce changes to a silicon surface, which include the appearance of periodic microstructures. A laser energy density of 12.0 J cm^{-2} has modified the surface of the sample.

The energy absorbed from the CO_2 laser beam is converted into thermal energy, which generates a series of effects such as melting, vaporisation of the molten material, shock waves in the vapour and in the solid, etc. Qualitatively, three zones on the silicon surface can be distinguished after laser irradiation: the central zone; inner periphery; the outer periphery. The modifications on silicon can be summarised as: nonuniform modifications (central zone); wave-like periodical microstructure (inner periphery zone); hydrodynamical structure-like droplets (outer periphery zone). The formation of the wave-like microstructures is discussed through the consideration of the LIPSS effect.

Wang et al. [10] have recorded the appearance of microstructures on silicon surface for the case backside coating. We obtained here, and in [9], the silicon surface modification, including the creation of microstructures, with no backside coating. Surface modifications were produced via the action of the shorter laser pulse length (about 2 μs), which is much shorter than in the work of Wang et al. [10], where pulse durations were between 30 and 80 μs. Generally speaking, refs. [9,10], and the present paper contribute to understanding the processes on silicon surface.

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