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SILICON SURFACE STRUCTURING BY XeCl EXCIMER LASER IRRADIATION IN ATMOSPHERIC CONDITIONS

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Surface structuring of silicon wafers has been done by irradiation with a XeCl (λ= 308 nm, τ_{FWHM} = 20 ns) excimer laser source in air at room and 100^0C temperature, respectively. Control of the surface texturization has been performed by variation of pulses number at the same laser irradiation parameters. We show that the uniformity of the structures induced by laser was significantly improved when a beam homogenizer was used. Micrometric size structures were induces by XeCl laser irradiation. Grating like ripples with a period approximately equal with the laser wavelength were observed only in the case of samples irradiated with 2000 pulses. Depending on the temperature of Si wafer, the damaging of the surface varied with the number of laser pulses. The optical reflectance decreased with the increase of laser pulses up to an average value of 10% for the sample irradiated with 6000 pulses at RT (room temperature). At higher number of pulses the reflectance increased slightly as a result of the damaging and redeposition of the material.

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1. Introduction

The use of lasers in micro-processing of materials like ceramics, polymers, semiconductors [1,2], etc. has attracted a high interest over the last decades and is continuously improving, using pulsed lasers in nanosecond or femtosecond regimes [3-6,10]. Surface texturing by laser irradiation modifies significantly the reflexions of the target [3,5]. Applications in solar cell industry would benefit from texturing since the surface contact between the incident light and the solar cell is increasing and the amount of the light reflected off is significantly reduced [5,6]. Most laser driven processes require vacuum systems [3], controlled ambient atmosphere [5], and/or auxiliary purging gases. Controlling the irradiation parameters in normal ambient atmosphere would be less expensive and more easily to be implemented in the technology. This work is a study on surface processing of Si (100) in normal atmospheric conditions. Silicon is often used in solar cell industry so that improved reflections are extremely important, mainly for obtaining the black silicon [4]. Many studies concerning the technology and the physics of laser processing of different materials were carried out [6-9]. The number and the duration of the laser pulses influence the features of surface texturing [3,10,11]. Longer pulses determine a larger heat affected zone (HAZ) [11, 12]. To date the femtosecond lasers are the most versatile tools for fine micro-processing with a minimum HAZ, but during this study we demonstrate that also the 308 nm excimer laser could be a reliable alternative.

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2. Experimental

The experiments were carried out on monocrystaline Si (100) double-side polished wafers used as targets, since this material is quite common in solar cell fabrication, thin film deposition and in LIGA technologies. No particular treatment has been applied to remove the native oxide from the silicon surface before laser processing. Prior to irradiations the Si wafers were successively cleaned into an ultrasonic bath in acetone, ethanol and deionized water for 15 min and then blown with high purity nitrogen. All the laser processing were developed in air. Before the irradiations the temperature of Si wafers was set at room temperature or heated at 100 °C by a ceramic heater with a temperature controller. For the latter ones the heating slope was 8^{o}C/min with a 5 min plateau at 100^{o}C before starting laser work. The temperature was held constant for entire duration of the experiment.

The surface morphologies following irradiation were investigated by scanning electron microscopy (SEM) with a Vega Tescan microscope and a maximum accelerating voltage of 30kV. The surface reflection measurements were performed with a spectrometer system manufactured by Avantes. All the reflectance spectra were recorded in the 200-1100nm wavelength range. The spot of the beam was around of 1 mm in diameter. The software used for measuring the reflectance spectra is TFProbe, produced by Angstrom Sun Technologies.

3. Processing set-up

Our system consists of an excimer XeCl Coherent Inc. LPX 220 laser source (λ= 308 nm, τ_{FWHM} = 20 ns). In all experiments, the laser beam was focused on the Si wafers at a laser fluence of 2.3J/cm^2 and a repetition rate of 100 Hz. In order to achieve laser beam uniformity better than 5%, a dedicated homogenizer system was used [13]. The homogenized laser beam was focused with a 5X demagnification optical system. Thus, a square mask of 15 mm wide was reduced at a square of 3 mm. In our experiments, the laser energy per pulse was kept constant at 300mJ while the temperature and the number of laser pulses varied. A motorized attenuator allowed us to control the energy per pulse variation. The schematic drawing of the set-up is given below:

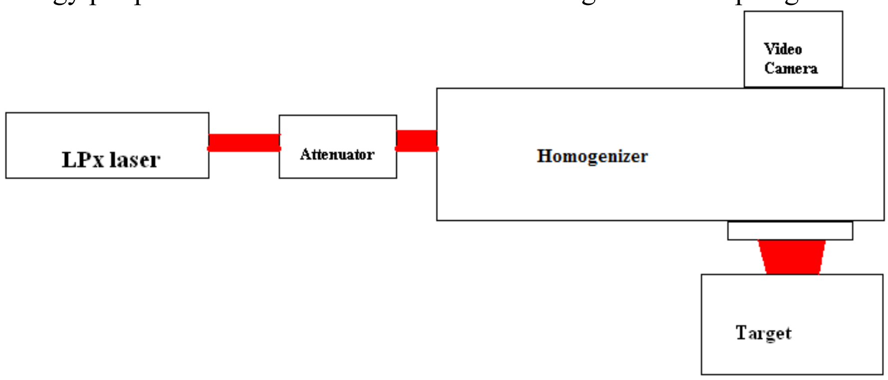

Fig.1 Schematic of the experimental set-up

The shape of the laser beam profile is conserved using an angular plate attenuator. Otherwise, the beam shape of the excimer lasers varies with the applied voltage, i.e. changing the output energy by simply changing the voltage. A quasi- linear dependence of the transmission coefficient with respect to the angle is obtained as can be seen in fig.2

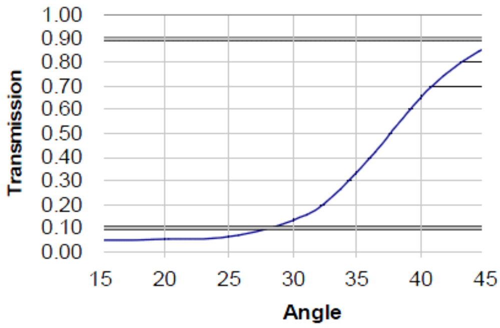

Fig.2 Transmission graph of the attenuator

Due to the different refraction index values, the laser beam is deflected on a different optical path than the optical axes of the system. A compensating plate was introduced supplementary to preserve the same optical path. The energy after the attenuator was kept constant at 210 mJ/pulse thus a laser fluence of ~2.3 J/cm^2 was obtained.

4. Results and discussion

In order to justify the role of homogenizer system we presented in fig. 3a the results on the irradiated Si wafer at the same fluence (2.3J/cm^2) by direct focusing of the beam. It is obvious that the non-uniform spatial distribution of the laser beam implies large differences between the central area, where the fluence is higher, and the peripheral regions. This result drove us to use a high performance homogenizer system. The homogenizer used in our experiments consists of two micro lens arrays disposed at 90 degrees, produced by Coherent Inc.

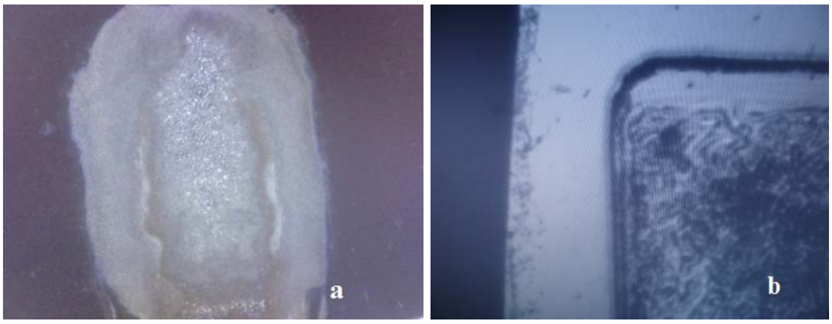

Fig.3 Optical image of Si wafer irradiated: a) without homogenizer and b) with beam homogenizer and squared mask

As it can be seen in fig.3a, in the case of laser irradiations without the homogenizing system, the spot on the target is not very well shaped compared with the spot obtained by using the homogenizer (fig.3b).

The first set of experiments were performed at 2.3J/cm^2 laser fluence, 100 Hz, 3 x 3 mm spot size, irradiation time between 20 to 80 seconds (equivalent for 2000-8000 pulses) without intentional heating of Si wafer. Keeping the same laser parameters and target temperature, the number of pulses was progressively increased from 2000 to 8000. A second series of irradiations were carried out at a Si wafer temperature of 100^{o}C, using the same laser parameters. The results are shown in figures 4-10.

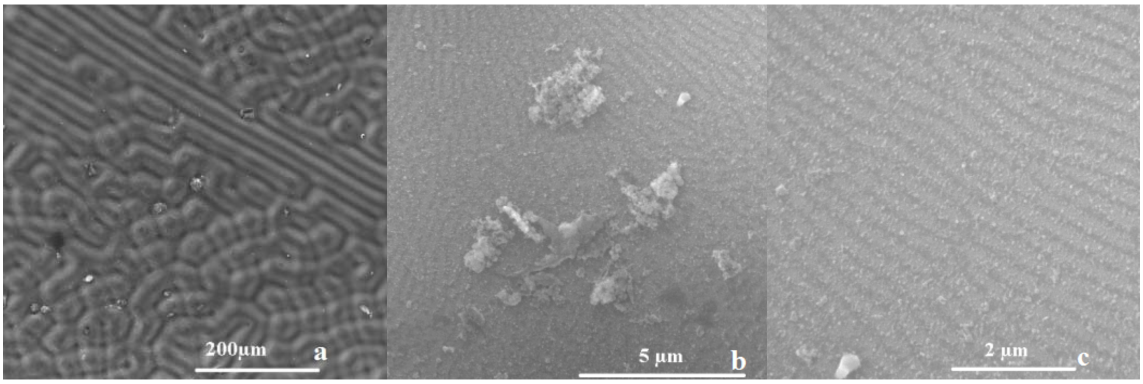

Fig.4) SEM micrograph of the Si wafer irradiated with 2000 pulses at RT

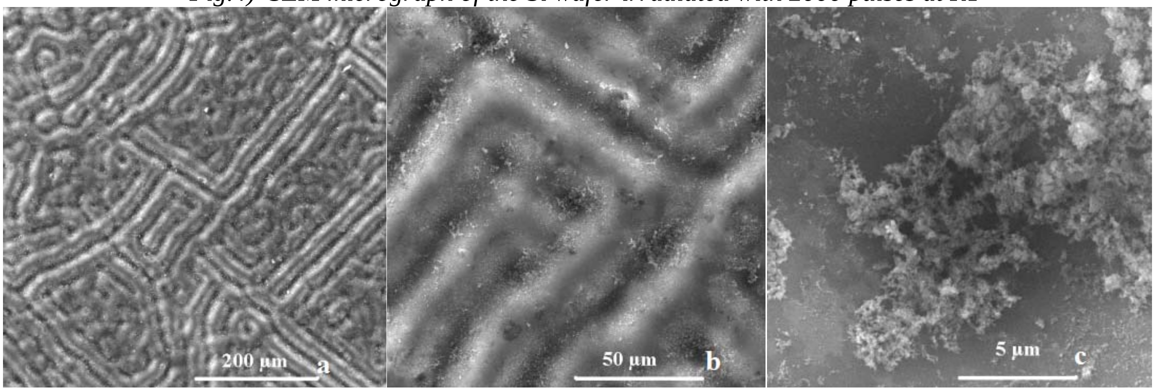

Fig.5) SEM micrograph of the Si wafer irradiated with 4000 pulses at RT

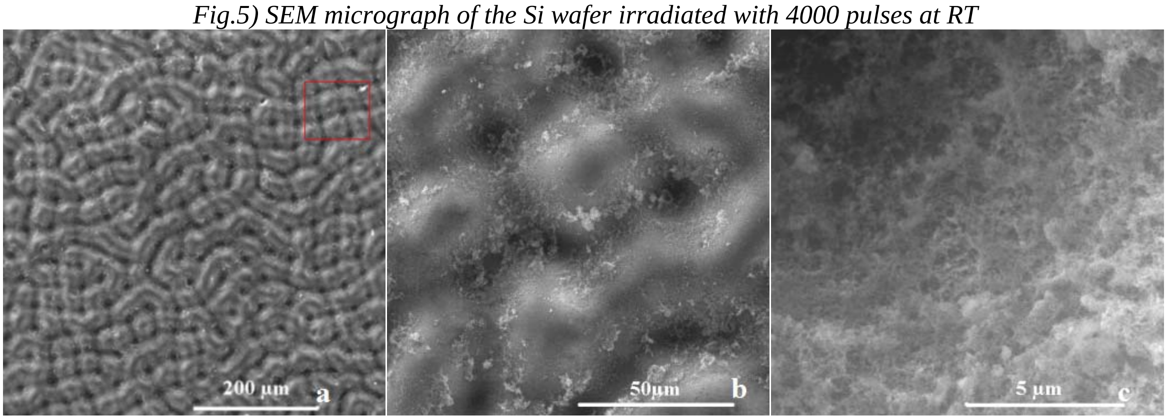

Fig.6) SEM micrograph of the Si wafer irradiated with 6000 pulses at RT

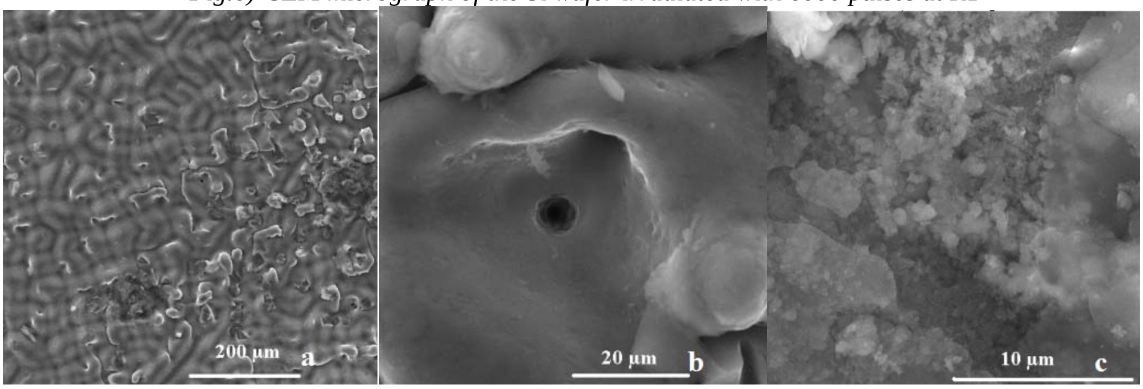

Fig.7) SEM micrograph of the Si wafer irradiated with 8000 pulses at RT

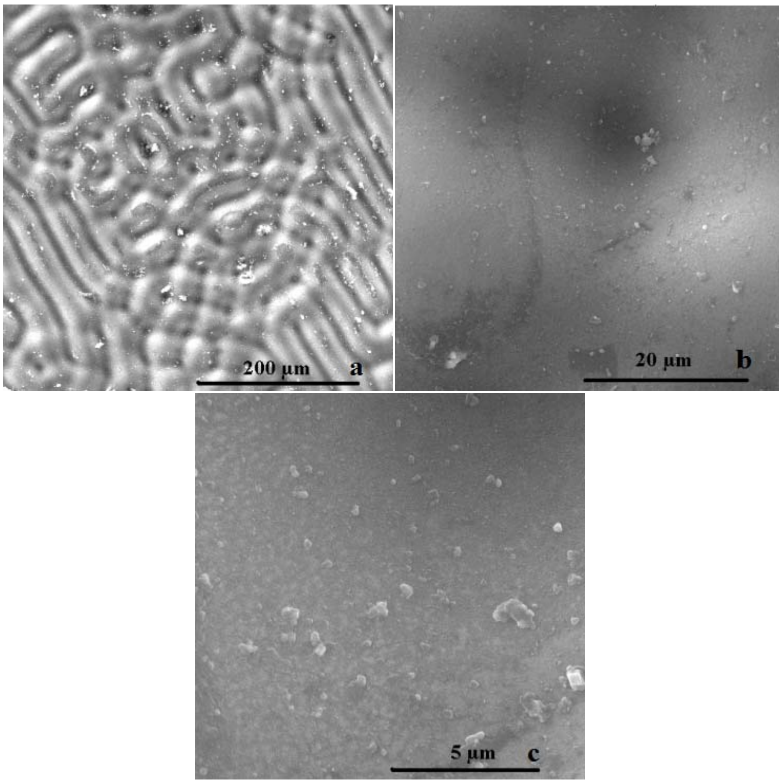

Fig.8) SEM micrograph of the Si wafer irradiated with 2000 pulses at 100°C

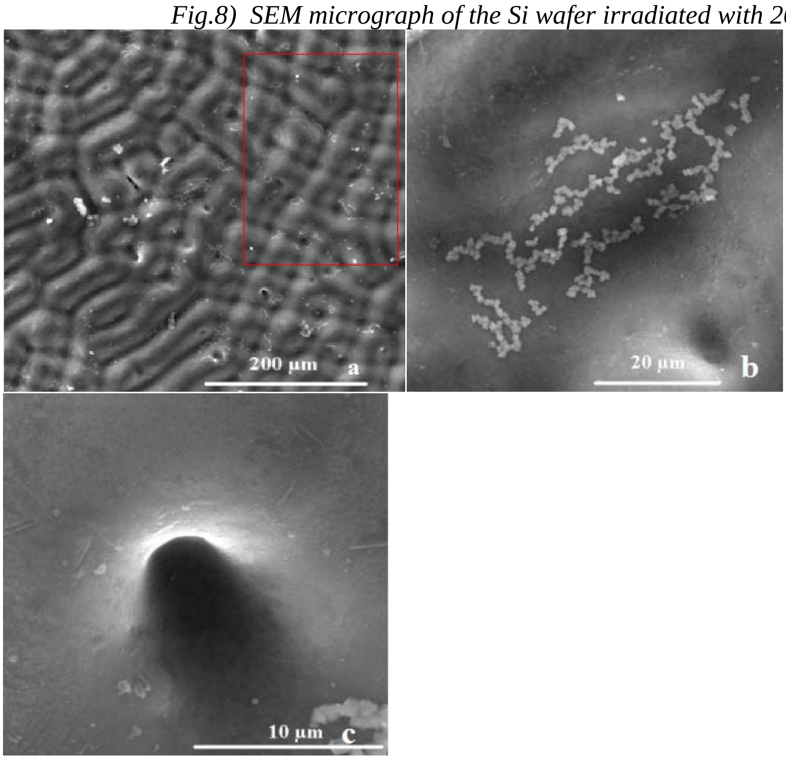

Fig.9) SEM micrograph of the Si wafer irradiated with 4000 pulses at 100°C

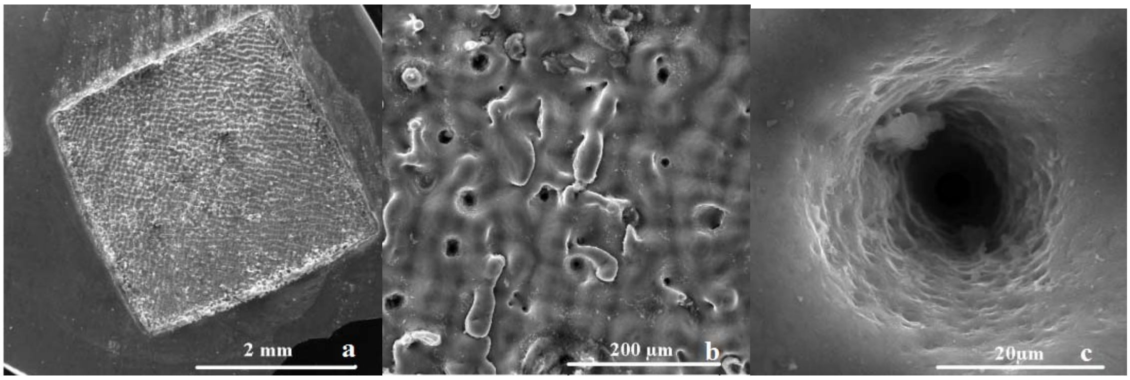

Fig.10) SEM micrograph of the Si wafer irradiated with 6000 pulses at 100°C

In the case of the sample irradiated with 2000 pulses at RT (fig.4), linear structures up to 500 µm length and ~40 µm width together with other random structures appeared. A similar behaviour was observed for samples irradiated with 4000 pulses whereas the induced structures were slightly tinner. When the number of applied pulses was increased at 6000, the linear structures disappeared and the independent aggregates with almost round shapes with a minimum diameter of 30-50 microns became predominant. It can be observed in figure 6a. that the structures are uniformly distributed on the whole irradiated surface. If the pulse number increased, the shapes become smaller in diameter, more rounded and separated. Similar structures were reported by laser surface texturization in vacuum [3] or in normal atmosphere [14], but not with homogenized laser spot. It is worth mentioning that in the case of Si wafer irradiated with 2000 pulses at RT, additional to the micrometric structures, grating like ripples with a period almost equal with the laser wavelength were observed (see fig. 4c). Such structures were obtained when the dielectrics or metals were irradiated with other laser wavelengths [15-18]. The samples texturized at 100^0C showed almost the same results as the samples irradiated at RT, but at a lower limit of laser number pulses for damaging of the surface. We considered the damaged surface, when the melted material is predominant. We found out that damaging of the surface occurred at lower number of pulses if the Si wafer was preheated, (e.g. 8000 pulses at RT - fig. 7 and 6000 pulses at 100^0C - fig.10).

Next step was to measure the modifications in surface reflection for the samples texturized at RT.

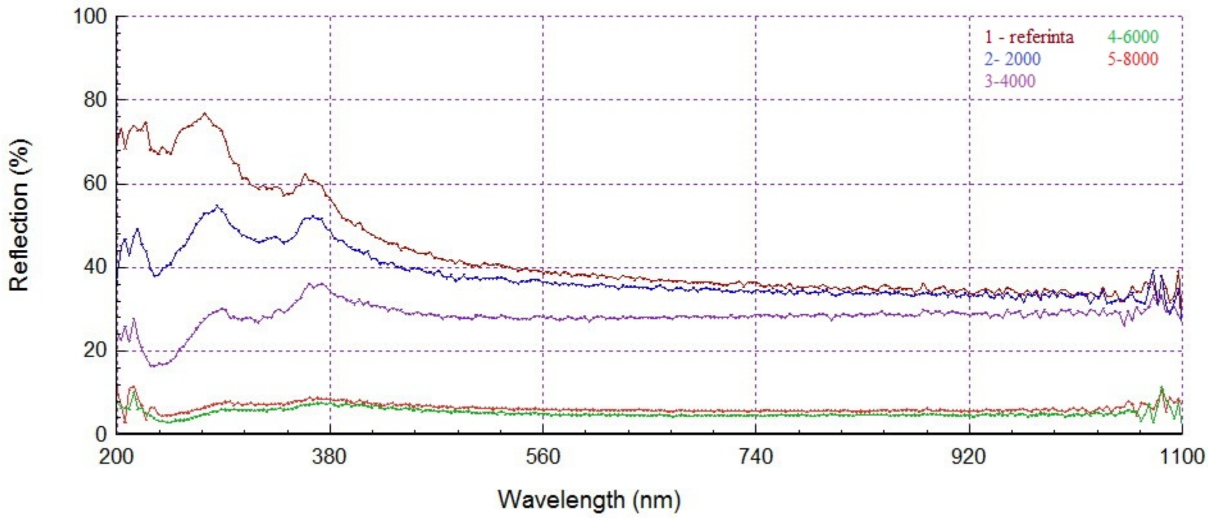

Fig.11 Reflection measurements on 1-Reference, non irradiated Si wafer; 2- Si wafer irradiated with 2000 of pulses; 3- 4000 pulses; 4 - 6000 pulses and 5 – 8000 pulses, respectively;

The reflectance spectra were recorded in specular geometry, by means of a bunch of optical fibers used for light source and detection. As reference, we used the fresh silicon surface before to be exposed to the XeCl laser pulses. The measurement of the reference (line 1) is similar to other results reported in the literature [5]. We can observe in fig. 11 that the optical reflectance of the structured Si wafer decreases with the number of pulses. With the increasing of number of pulses the structures become more numerous and thus the light is better trapped in the structured Si wafer. Before the irradiation the average reflectance measured in the UV range (200-380nm) is larger than 60% while in VIS-NIR is 35-45%. After irradiation with 2000 pulses, the reflectance in UV region decreases down to 50% whereas in VIS-NIR region only a slight decreased was observed. After 4000 pulses the reflectance strongly decreased to 30-35% on whole spectrum, however the profile of the curve remains the same. The best results were obtained when the silicon was irradiated with 6000 and 8000 pulses, thus the values of reflectance on the measured spectrum were lower than 10%. The optical reflectance of the sample irradiated with 8000 pulses slightly increased mostly due to the presence of the melted material on the surface which covers the structures.

5. Conclusions

Surface structuring of silicon wafers with XeCl laser generated an overall decrease of the optical reflectance with 30%. Thus, we evidenced the ability of a simple laser processing system to decrease the surface reflection by texturization with XeCl excimer laser. The features of surface patterns created by XeCl laser are dependent on the number of laser pulses. We established a regime for surface texturization with 308 nm radiation which can offer alternative for obtaining of the black silicon by a faster laser processing compared with fs laser approaches. Our experiments contribute also to a better control of the multi scale micro-processing by using high power UV lasers.

Acknowledgements

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