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Investigation and application of laser induced surface functionalization with pulse delays between 40ns and 50µs on silicon and steel foils

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Abstract

Laser induced quasi-periodic cone-like surface structures contribute to the functionalization of material surfaces. The resulting topography depends on manifold laser and ambient process parameters. In this study, the fundamental influence of a pulse delay between 40ns and 50µs has been investigated for the laser processing of silicon. During the processing, parameters of laser fluence and pulse overlap were set at constant condition used in the three laser systems. As the results, laser induced surface topographies are visualized by microscopy and analyzed with self-developed image processing tools to determine cone distance and cone density. The obtained knowledge from laser-induced quasi-periodic cone-like structuring helps to develop laser processes for various applications and materials, e.g. for photovoltaics or in medicine. In an exemplary case the surface functionalization is demonstrated for cathodes on steel foil.

Keywords: surface functionalization; quasi-periodic structures; pulse delay variation

1. Introduction

The optical, mechanical, and electrical properties of materials can be optimized for many applications by a tailored surface topology. As the example, the wettability of water on a metal surface can be controlled in both of hydrophilic and hydrophobic property reported by Fadeeva and Truong, 2011. The electrochemical performance of lithium cobalt oxide for Li-ion batteries is enhanced by an enlarge of reactive area with µm-

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sized cone like structures on the surface of the electrode, reported by Kohler et al., 2012. The organic electroluminescence (OEL), Shinar J. and Shinar R., 2008 and inorganic surfaces, Wu, 2002, can be also altered in optoelectronics via the surface topology.

A topology characterized by µm-scale surface features can be produced by laser ablation with distinct laser parameters and processing gases at different laser pulse durations, Li et al., 2011 and Overmeyer et al., 2013.

In this paper we report the generation, the analysis, and the modification of µm-scale surface features, the so-called quasi-periodic cone-like microstructures on silicon and steel foils induced by couples of laser pulses irradiated with delays between 40 ns and 50 µs.

This gained knowledge can be used to obtain the cone-like microstructures at optimized laser parameters on different materials and to apply them on cathodes.

2. Experimental and Analysis

2.1. Laser systems and setup

Three ultrashort-pulsed laser systems (USP) with laser wavelength of 532/515 nm were used for experimental investigation of functionalized quasi-periodic cone-like surface structures. Each laser system oscillates at different repetition rate, shown in Table 1. In the case of USP2, pulse trains can be emitted at a given repetition rate and a minimum selected pulse-to-pulse time interval of 40 ns, the so-called burst mode. The laser beam was scanned with a galvanometric scanner system and tightly focused with an f-theta objective lens onto sample surface. The laser parameters are adjusted to be geometrically constant in terms of laser fluence Φ as a function of pulse energy E_p and focal diameter d_{foc} at 1/e²

$$\Phi = \frac{4 \cdot E_p}{\pi \cdot d_{foc}} \tag{1}$$

and number of pulses per position N_{ppp} as a function of focal diameter, repetition rate f_{rep} and scanning velocity v

$$N_{ppp} = \frac{d_{foc} \cdot f_{rep}}{v} . \tag{2}$$

Table 1. Laser parameters of the used laser systems

system	USP1	USP2	USP3
parameters	Trumpf TruMicro5050	Coherent Rapid	Trumpf R&D
Pulse duration in ps	7	12	0.9
Max. pulse energy in µJ	60	28	6
Repetition rate in kHz	≤400	50/100 at ≥40 ns Burst	3500
Focal diameter at 1/e² in µm	24/30	30	27

The temporal time interval and the energy ratio for burst pulses have been measured by a photodiode. The pulse energy ratio between the first and the second burst pulse is obtained to be approx. 10:7.

2.2. Analysis of quasi-periodic surface microstructures

The geometric analysis of µm-scale structures (0.5 – 50 µm) can be executed with optical microscopy due to the small depth of focus in comparison to secondary electron microscopy. With this the image of the cone-like structures is focused only at one position in z-direction, so that the boundary of the cone-like structures is clearly defined for an automatized computer-based geometry evaluation. The analysis technique is based on 2D-Fourier image analysis. Three characteristic values are determined with this technique:

- the average distance Λ of quasi-periodic cone-like microstructures (see for graphical explanation quasi-periodical structures in Figure 2),
- the distance functional Ψ as a measure of the "structure density", and
- the spreading $\Delta\sigma$ of the quasi-periodic cone-like microstructures distance at a certain value. If all cones would have nearly the same distance between each other the spreading would be the cone density (blue line in Figure 1-Interpretation).

Furthermore the spreading is a measure for quasi-periodicity, e.g. Ripples have a small spreading around 50 nm and cone-like structures around 3 µm for silicon. The basic evaluation steps are shown in Figure 1.

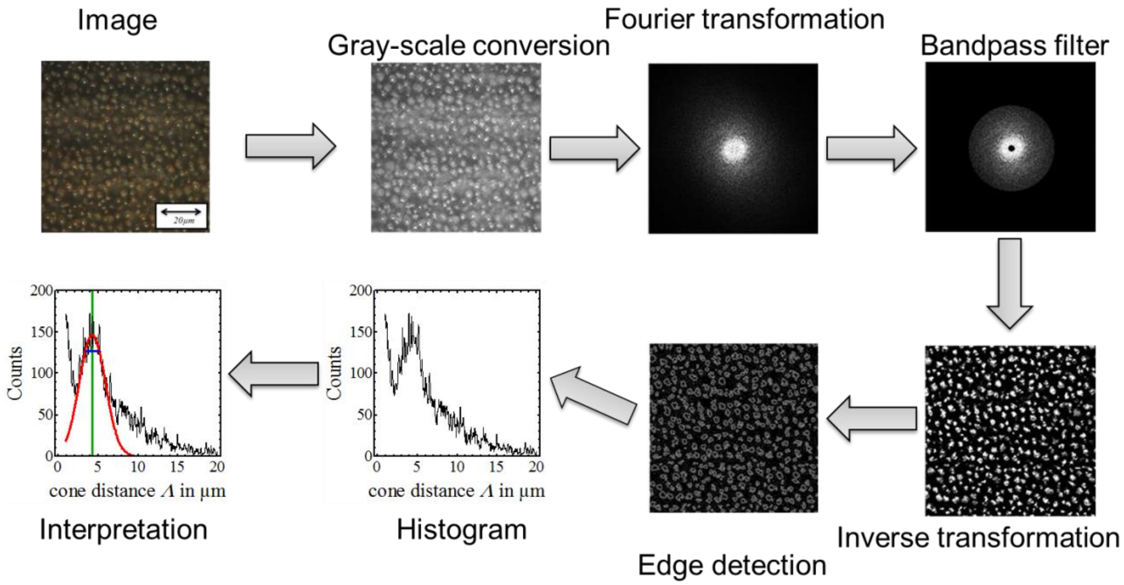

Figure 1. 2D-analysis scheme of periodic and quasi-periodic surface structures; analysis of quasi-periodic cone-like surface structures are shown; inlet "Interpretation": green line: average cone distance, blue line: spreading at 86.5 % of the peak value, red line: gauss fit to quasi-periodic cone-like structures, black line: distance distribution of cone-like structures, under the black line: distance functional

3. Results and Discussion

3.1. Fundamental investigations for silicon

Periodic and quasi-periodic surface structures can be observed in a wide range of process parameters. The typical shape of the laser induced surface structures are Ripples, e.g. Bonse et al., 2005, cone-like structures, e.g. Carey, 2004, and the transition state structures called here pearl-like structures, e.g. Sarnet et al., 2008, which are shown in Figure 2.

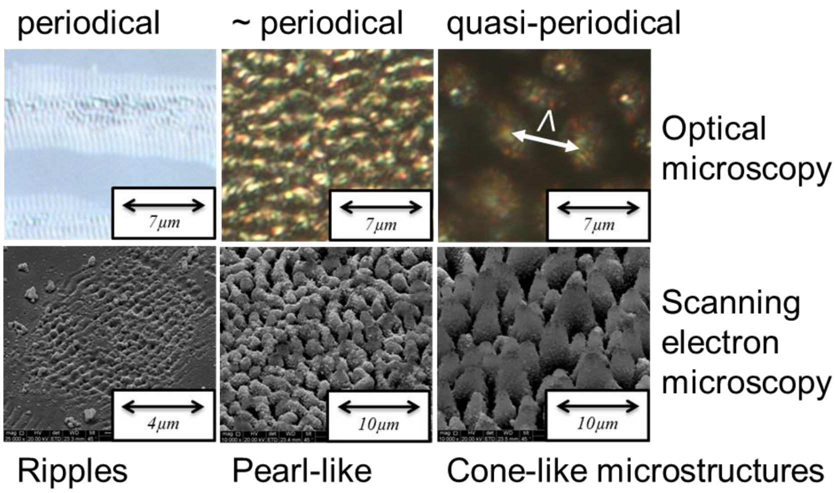

Figure 2. Laser-induced periodic and quasi-periodic surface structures

An upper estimation level for the average distance, shown in Figure 3 a, can be determined by the plasmonics described in Overmeyer et al., 2013 with the propagation length L_i, which is a function of n (refractive index), ε_p (permittivity), and a_p (ablation depth per pulse as a function of the material and laser fluence.The average distance of the laser induced cone-like structures increases as a function of ablation rate and laser fluence, respectively. The generation of laser induced microstructures, as shown in Figure 2, can therefore be classified with respect to their laser parameters by laser fluence and number of pulses per point. According to this theoretical description, the different laser parameters regimes for silicon are described in the following subsection and the av. cone distance and the distance functional as a measure for the “structure density” are shown in Figure 3.

Laser induced Ripples are observed on silicon at a laser fluence near the ablation threshold of 0.1 J/cm² and a few laser pulses per point. Up to a laser fluence of 0.3-0.4 J/cm² and up to 20-30 pulses per point pearl-like structures are generated on the materials surface. Laser induced quasi-periodic cone-like structures can be observed at fluences of up to 0.8 J/cm² and more than 30-40 pulses per point on silicon, see Figure 3 a. For larger fluences, a laser ablated groove occurs at the used laser parameters, see inlet in Figure 3 b. Ripples have not been observed at small laser fluences because of 100 pulses per point. The standard deviation has been determined for a laser fluence of 0.485 J/cm² to $\Delta\Lambda$ = 0.48 µm at a set of 15 samples, see Overmeyer et al., 2013. According to the increase of the average distance the distance functional, resp. “the structure density”, decreases and stays stable for laser induced grooves above a laser fluence of larger 0.8 J/cm², see Figure 3 b.

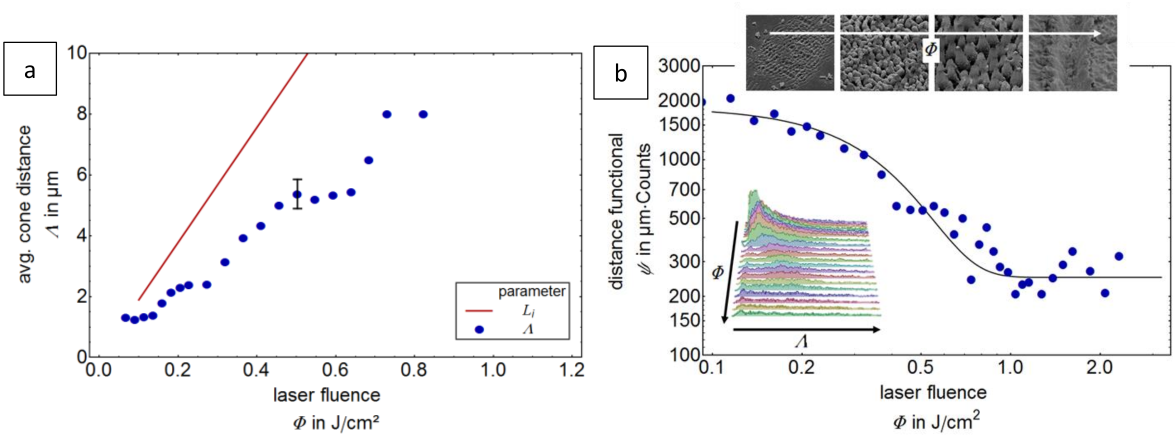

Figure 3. a) Height and average cone distance of pearl- and cone-like structures as a function of the laser fluence for Si <111>; USP1, repetition rate 400kHz, focal diameter 24 µm, 100 pulses per point; standard deviation determined to be $\Delta\Lambda = 0.48$ µm; red line: propagation length of surface plasmon polaritons, Overmeyer et al., 2013; b) Distance functional of the single cone distance distributions (multi-coloured inlet); USP1, repetition rate 400kHz, focal diameter 24 µm, 100 pulses per point; black line: to guide the eye

Further, the generation of quasi-periodic cone-like microstructures depends on the time interval between two laser pulses, i.e. the repetition rate and/or the time interval between two pulse bursts. The effect of the repetition rate during laser processing on cone-like structures can also be demonstrated by the change of the spectral reflectivity, reported in Schütz et al., 2014. For small temporal pulse intervals, the quasi-periodic structures are destroyed due to thermal effects like melting, see molten structures in the following Figure 4.

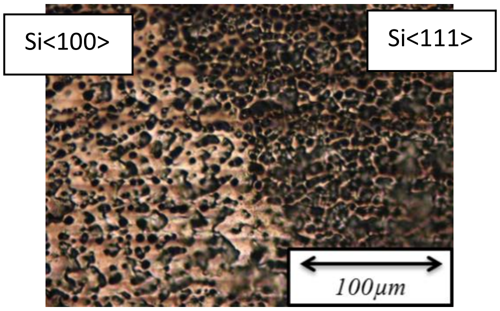

Figure 4. Multicrystalline silicon after laser processing with USP3

Increasing this temporal pulse interval reduces the thermal load on the material. For larger temporal pulse intervals, less melting has been observed at the three investigated laser fluences. The transition from thermal influenced to laser induced cone-like structures can be seen in Figure 5. A large distance functional, resp. “the structure density”, at a small temporal pulse interval is achieved with many thermal influenced and partly molten structures, which are detected during analysis as highly dense small circles. A smaller distance functional at larger temporal pulse intervals is achieved with less molten structures and more distinct cone-like structures. The transition from more molten surface structures to more distinct cone-like structures can be seen for two different grain orientations on Si<100> and Si<111> in Figure 6 a with the decreasing slope at temporal pulse intervals around 500 ns. For longer pulse intervals or lower repetition rates, the topology does not significantly change. This is shown with the average cone distance as a function of the laser fluence at different repetition rates in Figure 6 b. Laser processing with low repetition rates induces a larger oxidization of the surface, discussed in Schütz et al., 2014, despite the fact that the average distance does not change, see Figure 6 b.

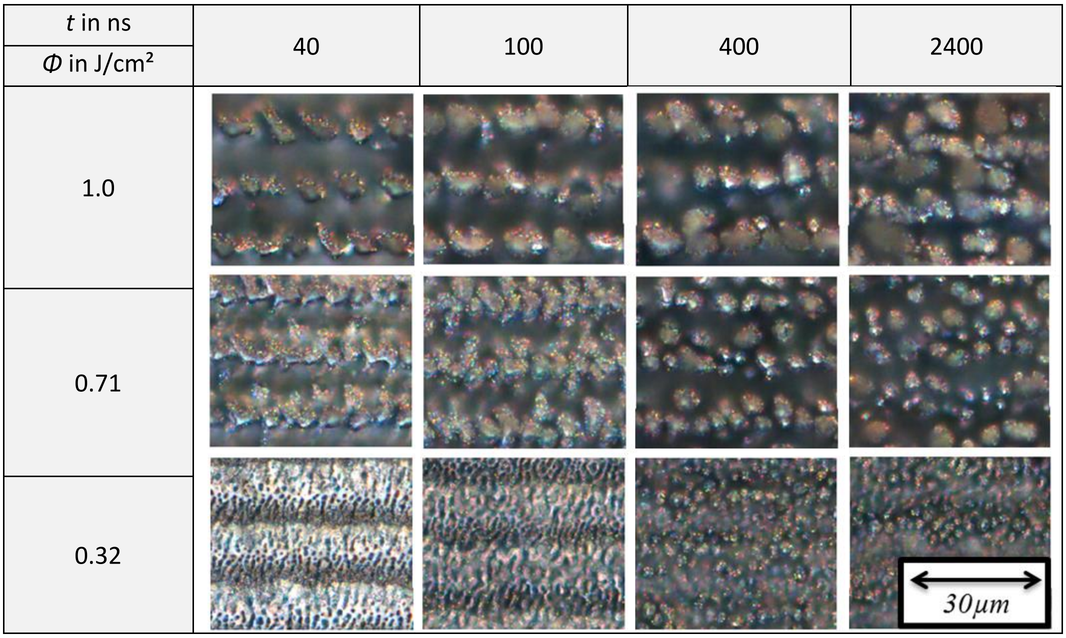

Figure 5. Toplogy of quasi-periodic cone-like microstructures as a function of pulse time delay and laser fluence; Si<111>; USP2; repetition rate 50kHz, focal diameter 30 µm, 50 pulses per point, Schütz, 2015

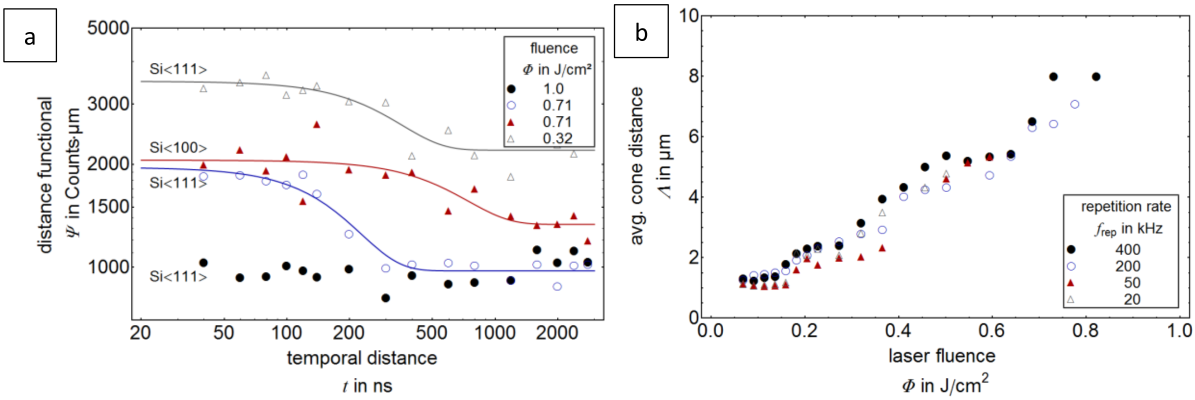

Figure 6. a) Distance functional of the inlets in Figure 5; Si<111> and Si<100>; USP2; repetition rate 50kHz, focal diameter 30 µm, 50 pulses per point; lines to guide the eye; b) Average cone distance of pearl- and cone-like structures as a function of the laser fluence at different repetition rates for Si <111>; USP1, repetition rate 400kHz, focal diameter 24 µm, 100 pulses per point

3.2. Investigations on steel

With the obtained knowledge appropriate laser parameters could be quickly determined for the structuring of 200 µm thick CrNi-steel foils. The appropriate laser parameters for CrNi-steel foil listed in Table 2 do not significantly differ from that of the Si substrate. Figure 7 shows (a) macroscopic, (b) microscopic optical images of typical quasi-periodic cone-like microstructures on CrNi-steel foil and (c) their histogram of the cone distance, respectively. The obtained surface morphology indicates little melting and deformation due to thermal effects.

Table 2. Laser parameters to achieve a quasi-periodic cone-like microstructure on CrNi-steel foils

parameters	USP1
Pulse duration in ps	7
Max. pulse energy in µJ	5-8 @ 267 pulses per point
Repetition rate in kHz	400
Focal diameter at $1/e^2$ in µm	30

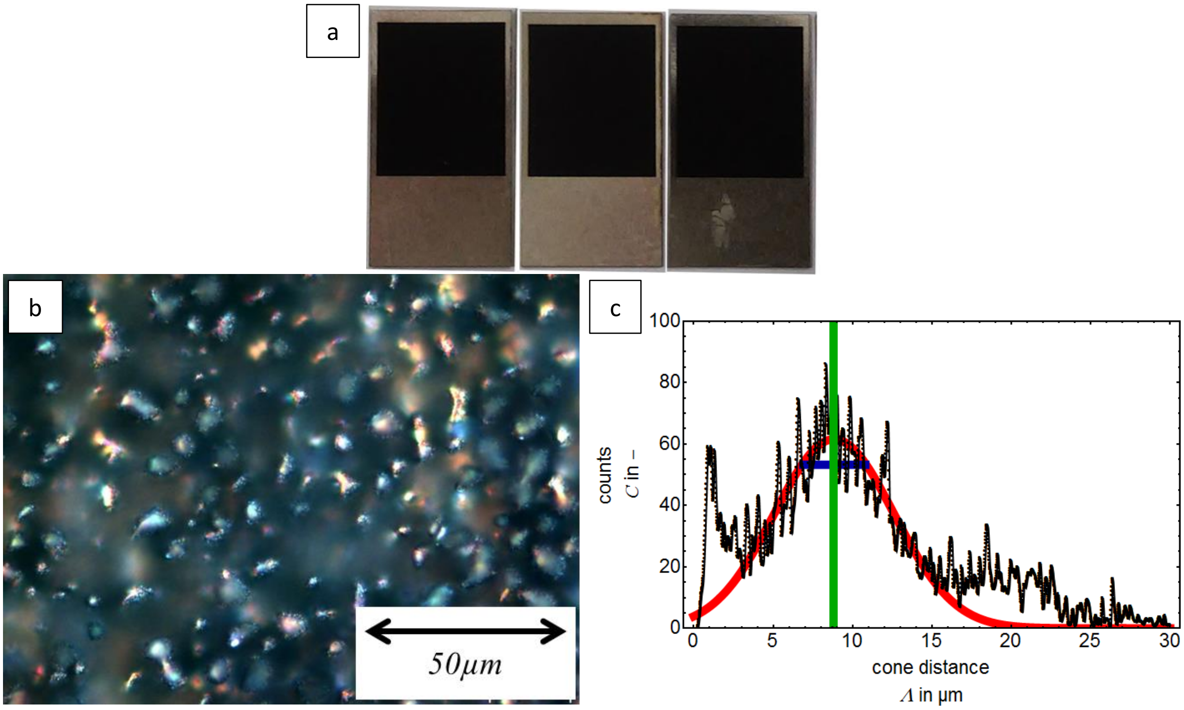

Figure 7. a) Macroscopic appearance of quasi-periodic cone-like microstructures on CrNi-steel; b) Laser induced quasi-periodic cone-like microstructures on CrNi-steel; c) Histogram of the c one distance of Figure 7 a

The enhancement of effective surface area by such cone-like topology can be expected to be used as cathodes for various applications and is currently under investigation.

4. Summary and Outlook

Quasi-periodic µm-scale cone-like microstructures can be induced and altered by laser radiation. These structures are used for various applications. It is possible to change the topology of the cone-like structures drastically by changing the time interval between two laser pulses. In case of short time delays nearly no cone-like structures are formed. Above a certain material and laser energy parameter dependent time delay threshold, the structures are formed and stay nearly geometrically equal. Increasing the time delay further with e.g. lower repetition rates yields a more visible macroscopic oxidization of the surface.

This gained knowledge on the evolution of laser-induced quasi-periodic cone-like structures helps to develop laser processes for various applications and materials, e.g. for photovoltaics or in medicine. In an exemplary case the surface functionalization is demonstrated to be implemented for cathodes on steel foil.

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