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# UV – surface treatment with 248 line beam system for large-scale production

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### Abstract

In large-scale production, reducing the processing time while maintaining high precision is of crucial importance in order to reduce production cost and guarantee high quality. To achieve this aim, a line beam system combined with a 150 W excimer laser as the beam source is introduced. UV excimer laser radiation has proven itself for precise structuring and modifying of micro- and nanometer-scale layers. With the 248 nm excimer laser, materials can be selectively modified with a depth resolution below 0.1 micrometers. Due to the latest technical development, high power excimer laser bridges the gap between high precision and cost-efficient processing. The linear beam concept dispenses with movable components such as scanner optics. By using a fixed line beam with nanosecond pulse duration, a system with optimum reproducibility has been developed. Depending on the application, the radiated beam can be shaped by an optical mask design. This machine's modular concept can be used for a wide range of materials and laser-processes, especially for large-area applications. One example is the ablation of matrix material in carbon fiber-reinforced polymer materials for the aviation industry.

Keywords: Excimer laser; Line Beam; laser-induced ablation; CFRP

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### 1. Introduction

UV excimer laser radiation has proven itself for processing and modifying micro- and nanometer-scale layers. As the only native UV laser technology, excimer lasers are the only practical source of high power UV laser light. Hence, UV excimer lasers are predestined for large-scale processes, which is mainly used in display manufacturing. Their unique characteristics have rendered them enabling in a number of high precision fabrication tasks, especially in smartphone and display manufacturing. Continuing improvement in the quality, reliability and output characteristics of excimer lasers, necessary to meet today's demanding applications, have established this powerful UV technology on the forefront of industrial laser micro-manufacturing (Delmdahl, R., 2010). Since short-wavelength excimer layers have a low optical penetration depth and short pulse duration, they exert negligible thermal influence on the components and are, thus,

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qualified for the gentle functionalization of thin layers of all types of conductive, semi-conductive or insulating materials.

In order to transfer these properties to different coating systems and a large product range, the Fraunhofer Institute for Laser Technology ILT, in close cooperation with Coherent, operates a novel 248 nm UV laser line beam system in Aachen. This system provides the technological basis for developing innovative surface functionalities and new products and expand the application field for large-scale production.

With the 248 nm excimer laser approach materials can be selectively modified with a depth resolution below 0.1 micrometer. Moreover, it enables users to precisely structure sensitive multilayer systems without causing thermal damage. The functionality of the short wavelength line beam system and the attainable layer quality are evaluated for the ablation of matrix material in carbon fiber-reinforced polymers (CRFP). Based on these experiments, new industrial laser processing applications for the UV laser line beam system are identified.

## 2. Characterization of the Line Beam system

The Coherent LEAP excimer laser delivers stabilized output power of 150 W at 1 Joule stabilized pulse energy (typ. 0.5 %, sigma) and 150 Hz maximum repetition rate, respectively. Together with superior beam homogeneity, the Line Beam system ensure accurate and reproducible thin film deposition results. At a typical laser discharge unit lifetime of 6 billion shots, a LEAP/Line Beam system (see Fig. 1, left hand side) can be operated in volume production over the course of several years with minor routine maintenance actions such as automated gas fills after every 30 million pulses (see Fig. 1, right hand side) corresponding to over 60 hours consecutive stabilized pulsed laser operation at 150 Hz. These numbers are achieved by employing the latest maintenance-free semiconductor-switched tube technology, which enables a particularly even and effective gas discharge over billions of laser shots.

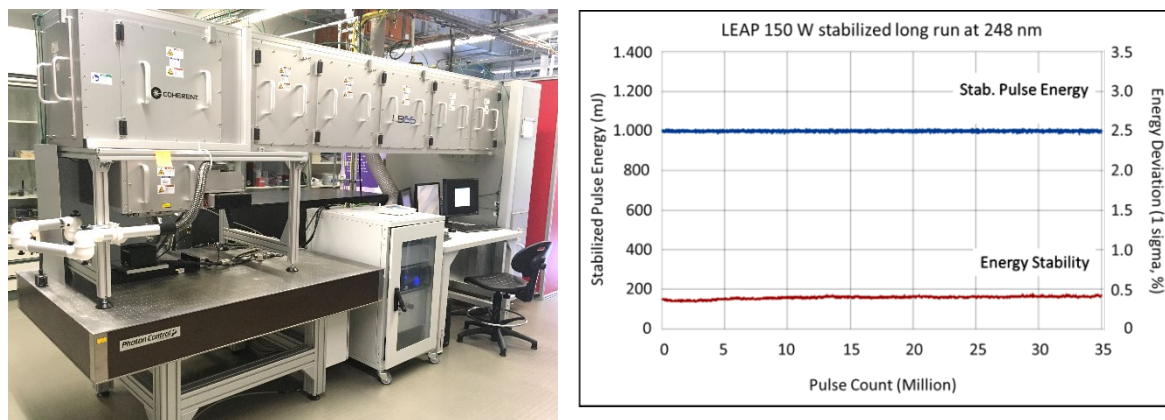


Fig. 1. On the left hand side, the UV laser line beam system is shown. On the right hand side, the long-term pulse energy stability of 35 million pulses at 1 J (blue line) and the energy deviation (red line) are presented.

The beam projection design of the 248 nm line beam system provides a unique 1.2 J/cm<sup>2</sup> fluence in the substrate plane and a nominal beam size of 155 mm in length. In order to ensure the optical system's longevity, it is made exclusively of specially selected high-quality substrate and coating material for all of the optical components to of withstanding the 248 nm photons at the high 150 W UV power. Moreover, a novel

illumination concept has been designed which greatly reduces the energy density on all UV optical components and the beam homogenizer in particular.

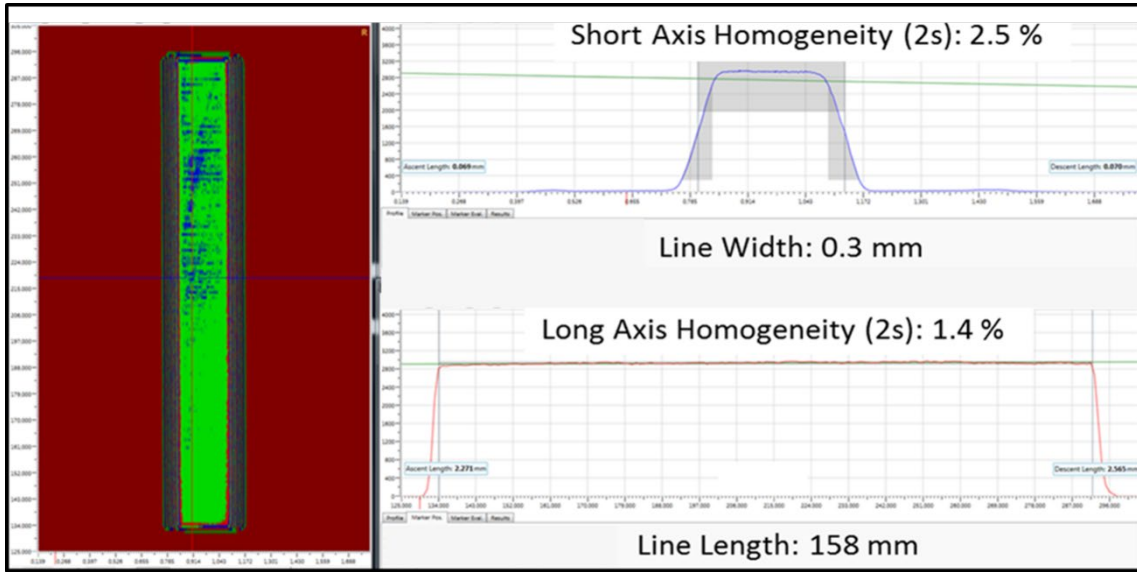


Fig. 2. False color CCD camera image of the line beam 155 and the respective top-hat profile cross sections obtained along the short beam axis and the long beam axis (Delmdahl, 2019).

In Figure 2, a two-dimensional CCD camera image of the line beam recorded in the substrate plane is shown together with the cross sections obtained along the short beam axis and the long beam axis, respectively. It is clearly seen from the cross sections that both the short and the long beam axis are shaped into a flat-top profile. Two sigma homogeneity values of 2.5 % for the short axis and 1.4 % of the long axis are easily achieved with the LEAP line beam system. The slight flat-top tilt which is visible in the short axis cross section can be deliberately adjusted from positive to negative angles in order to optimize laser material interaction during ablative scanning applications. On the basis of a 1 Joule per pulse excimer laser output as provided by the LEAP and taking into account the overall optical efficiency of the line beam system of nearly 70 %, a line length of 158 mm (FWHM) (nominal value of 155 mm) and a line width of 0.3 mm (FWHM) with a homogeneous maximum fluence of 1.2 J/pulse is achievable (Delmdahl, 2019).

One of the most important factors determining the reproducibility when selectively processing thin films on larger substrates is the depth-of-field of a laser system. Due to the high pulse energy of 1 J/pulse available from the LEAP excimer laser, the LEAP/line beam 155 imaging system is designed with low numerical aperture resulting in a very high depth-of-field of  $\pm 100 \mu\text{m}$ . In figure 3 (left hand side), the short axis width versus the long axis beam position has been measured for three height positions  $z$ . The FWHM short axis width remains unchanged for variations of  $z$  between  $-100 \mu\text{m}$  (focus plane below the substrate plane) and  $+100 \mu\text{m}$  (focus plane above the substrate plane).

In fact, changing the substrate plane in vertical direction relative to the line beam focal plane results in a line width change of less than 2 % when measured at 50%, 90% and 96 % short axis width levels. Substrate height variations during panel scanning on the production floor are thus largely unnoticed. The three-dimensional energy distribution of the 155 mm line beam geometry in the substrate plane is shown for completeness in figure 3 in the right hand side.

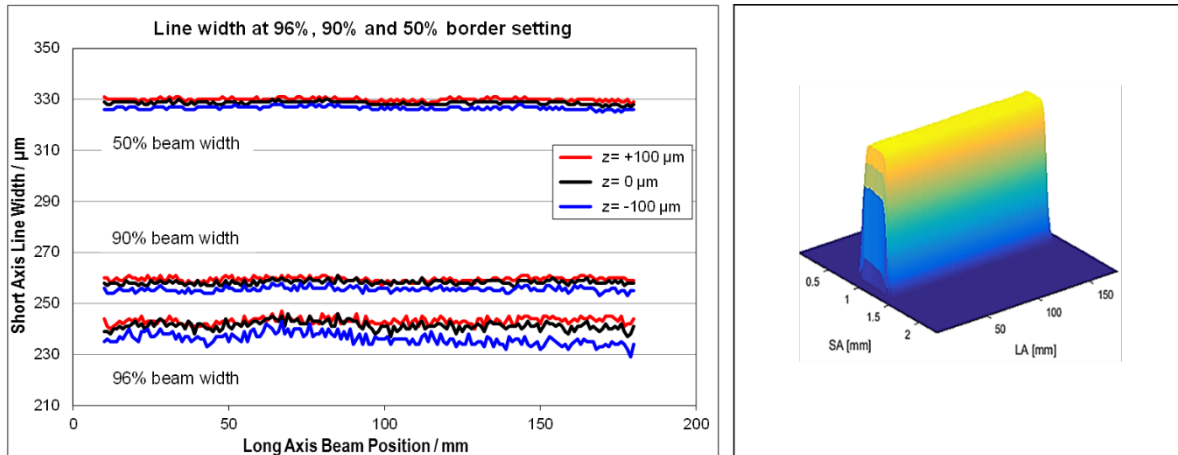


Fig. 3. Short axis line width recorded as a function of shifting the focus position (left hand side) and corresponding 3D energy distribution measured in the substrate plane at relative focus height position  $z=0 \mu\text{m}$  (right hand side).

In general, the beam delivery technology of the 248 nm line beam system can be designed to provide different line lengths and width combinations all the way up to square field geometries, in order to perfectly align with substrate sizes or thin film dies and patterns.

### 3. Laser-induced ablation of Matrix material in Carbon Fiber-reinforced polymers

One exemplary application for large-scale excimer laser processing is the ablation of matrix material in carbon fiber-reinforced polymers (CFRPs). This is in particular interest for the aviation industry. Since the aviation industry requires for new technology in order to make air traffic more functional, efficient and environmentally sustainable, the use of aerospace components made of CFRP is becoming increasingly important. The reduction of weight, while maintaining the same mechanical loadbearing capacity, leads to fuel saving and as a result to a cost reduction. Today CFRP are the baseline for aircraft primary structures, providing higher strength to weight performance, better fatigue strength, and potential to offer greater freedom of design (Hexcel Reg. Trademark, 2013).

Due to high manufacturing tolerances, the CFRP components lack of high precision which leads to assembling challenges of large aircraft primary structures (F. Ehmke, S. Rao and J. Wollnack, 2017). To avoid joining gaps, the primary structures are produced larger than required and afterwards selectively reduced in size. This ablation process is called "shimming" and can be precisely carried out by an excimer laser system. A sensor system identifies excess material which is then laser-induced ablated (compare Fig. 4). Thermal or mechanical damage of the CFRP aircraft component must thereby be avoided, since these materials are cost-intensive and have to perform under high mechanical demands.

Another subsequent processing example of CFRP is the sensor integration, which is also sketched in figure 4. The requirements for the damage-free ablation process of the matrix material are the same as

before. To locally ablate the matrix material of CFRP, the UV-laser source line-beam system in combination with a mask-based optical design is introduced. With a subsequent metallization process of the carbon fibers, sensor technology for aerospace components can be integrated into the structure. The nanosecond pulses can be specifically modulated for the required temperature range. Due to the wavelength of 248 nm, the penetration depths are very small, enabling precise ablation of the surface-near matrix material without damaging the carbon fibers.

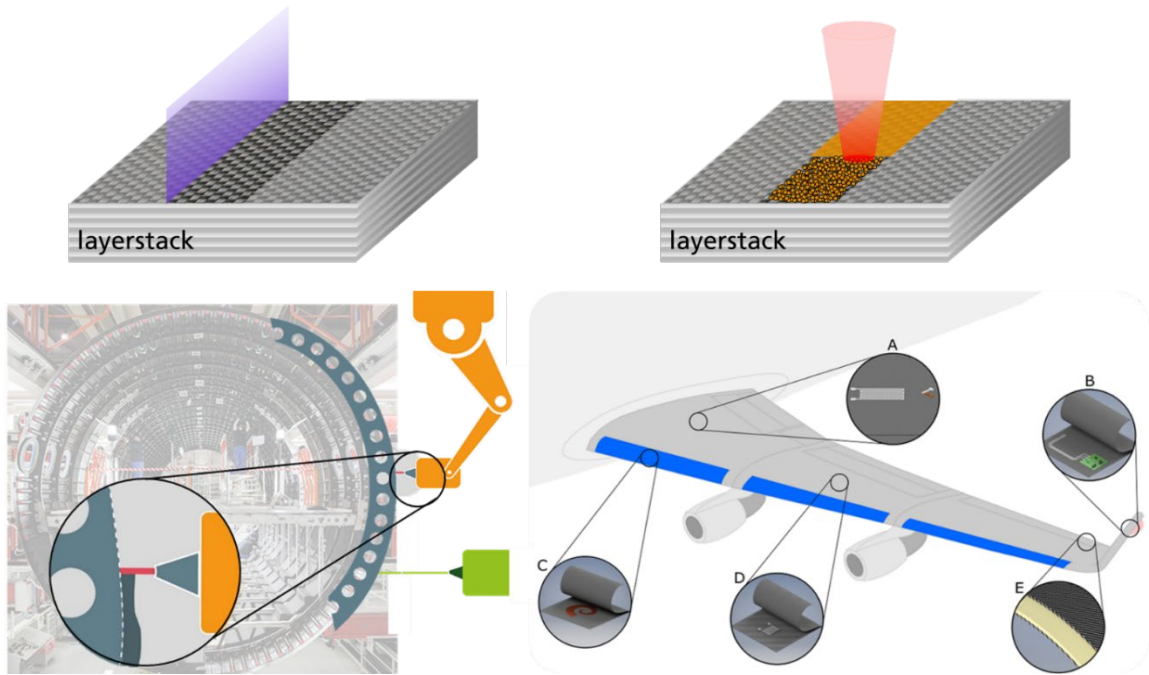


Fig. 4. Laser ablation process of matrix material in CFRP structure. Alternatively, the exposed fibers are subsequently metallized for sensor integration (Ohle, M., 2017).

### 3.1. Composition of carbon fiber-reinforced polymers

The essential constituent of the CFRP materials are the carbon fibers. Carbon fibers are made out of precursor fibers, which are first stabilized, then carbonized and, depending on the material and the mechanical demands, finally graphitized (Yin Y., et al., 1994). The carbon structure of the fibers is in theory a graphite structure with separated graphene layers. The orientation of the layers is along the radial symmetric axis of the fiber and, depending on the material, circularly or radially disposed. However, in reality, there are defects inside layers and crosslinks between the different layers leading to a so called turbostratic structure after the carbonization process. On the one hand, these crosslinks strengthen the connection between the layers, but on the other hand, this causes the fibers to harden resulting in less elasticity and mechanical demand.

To reduce defects and increase the mechanical properties, the fibers are additionally heat treated in an argon inert atmosphere. This is called the graphitization process, in which the oxidation quantities of the fibers are reduced due to recombination of carbon atoms to the graphite structure. As a result, typical values of the oxidation quantity range from 0.5 to 1.5 % volume fraction, which is about five times smaller than

after the carbonization process (Yin Y., et al., 1994). Finally, the fibers are surface treated with an adhesion promoter which is called “Sizing” to increase friction with the matrix material and to protect the fiber of environmental influences. The fibers are brought together to form fiber bundles. These bundles consist of 1000 to 24000 fibers. Depending on the mechanical demands, the bundles are then woven to carbon fiber-layers.

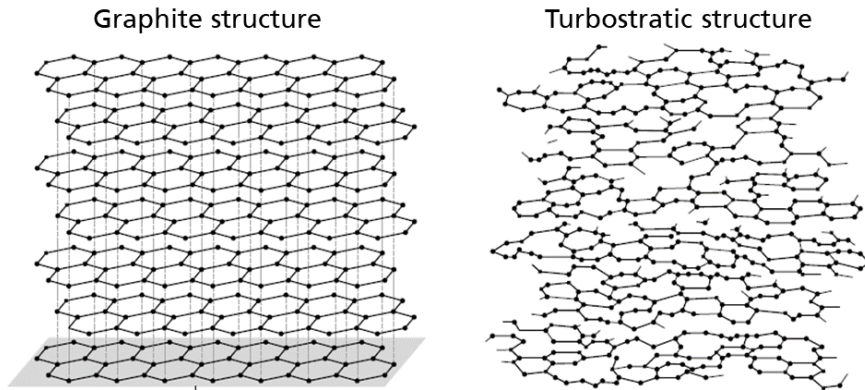


Fig. 5. Image of the graphene structure inside of carbon fibers. Left hand side: Theoretical and ideal graphene structure. Right hand side: Real structure including defects and crosslinks resulting in a turbostratic structure (Schimmelpfennig, S.; Glaser, B., 2012).

The irradiated material in these experiments is Hexply M21. It consists of an epoxy matrix supplied with 14 carbon fiber-layers, each about 400  $\mu\text{m}$  thick, in a plain weave structure as shown in figure 4. The material is primarily used for aerospace structures and provides high toughness and residual compression strength as a result of the plain weave structure causing low drapeability and high crimp (Hexcel Registered Trademark, 2015).

### 3.2. Laser ablation mechanisms

The laser-induced ablation itself can be distinguished between two different ablation mechanisms: the photo-induced and the thermal ablation. Due to ultrashort pulses and high energies, the material in the photo-induced ablation is laser-based vaporized. This ablation process is more precise resulting in higher resolution of structuring and in the reduction of thermal load inside the workpiece. In the case of the thermal ablation, additional processes, like heat diffusion and melt pool dynamics, decrease the precision of the process (Poprawe, R., 2011). Depending on the amount of energy and pulse length, a melt pool is induced forming droplets as sketched in figure 5. In this kind of process, the energies are smaller compared to the photo-induced ablation.



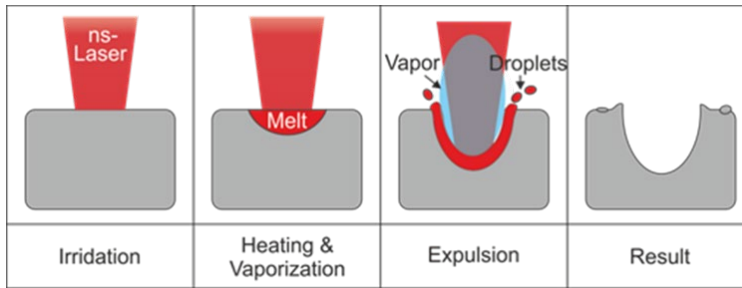


Fig. 5. Process relevant mechanisms of the laser-induced ablation. A vaporization as well as melt pool dynamics is sketched.

### 3.3. Ablation Process CRFP

To avoid thermal damage or mechanical damage, qualified parameters for the laser-induced ablation process of the epoxy matrix have to be identified. The limiting temperature in the laser-induced ablation process of CFRP matrix material is determined by the oxidation behavior of the carbon fibers. The first oxidation effects are observed at temperatures of 300 °C (Cherif, C., 2011). However, due to short interaction times in the laser-induced ablation process, the critical temperature of relevant carbon fiber oxidation is at about 800 °C (Yin Y., et al., 1994). This temperature range is referred to the thermal ablation. The decomposition temperature of the used matrix material Hexply 21M is at approximately 425 °C (Tranchard P., 2017).

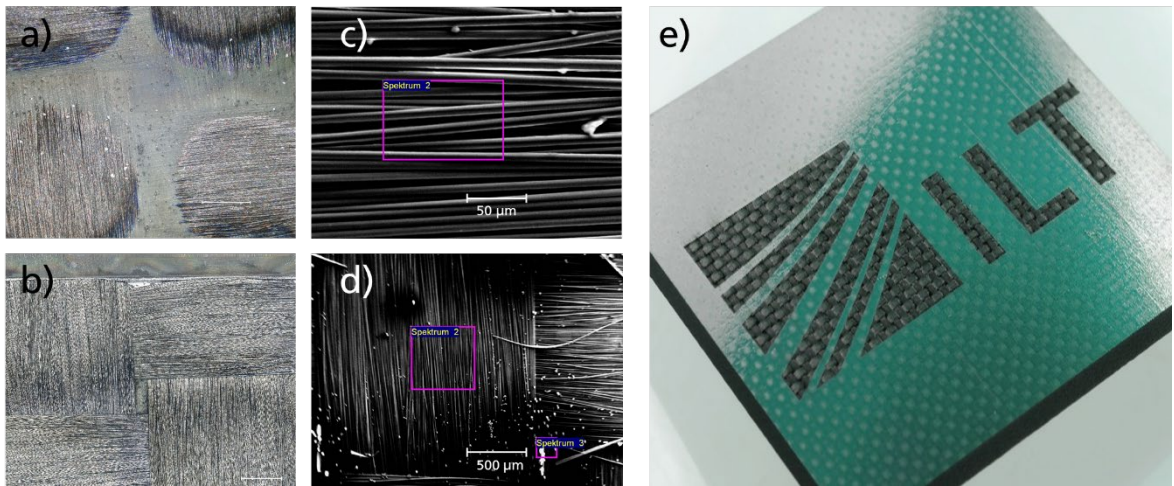


Fig. 6. Laser scanning microscope (a – b) and scanning electron microscope images (c – d) for different parameter sets. On the left side, a whole sample which is surface treated with by a mask-based optical system is shown.

Therefore, a parameter investigation is carried out varying the intensity from 0.24 to 0.97 W/cm<sup>2</sup>, the scan-velocity from 1 to 2 mm/s and the number of repetitions. The results are analyzed by laser microscope (LSM) and scanning electron microscope (SEM). The size of the parameter fields is kept constant with 5 mm x 10 mm as well as the pulse repetition rate with 150 Hz.

To identify mechanical damage of the carbon fibers and the ablation depth of the matrix material, an investigation with the LSM is carried out. As an example, two different images are shown in figure 6: a) with an intensity of  $0.24 \text{ W/cm}^2$ ,  $1 \text{ mm/s}$  scan-velocity and 4 repetitions; and b) with  $0.48 \text{ W/cm}^2$  intensity,  $1 \text{ mm/s}$  scan-velocity and 8 repetitions. In both images, exposed carbon fibers can be identified, whereas in a) there is still matrix material left between the bundles. Due to the woven structure of the bundles, the carbon fibers have a periodic height distribution which varies within  $35 \mu\text{m}$  from the lowest to the highest point detected. The first carbon fibers are exposed at an ablation depth of  $6 \mu\text{m}$ . Therefore, ablating the epoxy matrix further than to a depth of  $6 \mu\text{m}$ , the carbon fibers and matrix material are simultaneous irradiated. To avoid any oxidation process of the carbon fibers, the applied intensities have to be adjusted, so that the resulting temperatures are below the oxidation temperature of about  $800^\circ\text{C}$ . At intensities higher than  $1 \text{ W/cm}^2$ , a discoloration can be recognized indicating an oxidation process. Therefore, the applied intensities are below that mark resulting in a thermal ablation process. This can also be recognized by small dots indicating melt pool dynamics.

In order to obtain exposed carbon fiber structures only, the matrix material has to be ablated down to a depth of  $41 \mu\text{m}$  (Fig. 6 b). To verify the degree of oxidation, an energy dispersive X-ray spectroscopy for chemical analysis with SEM is carried out. The images of two different areas are shown in figure 6 c) and d). In these images, there is also no mechanical damage observed. Small droplets by melt from the matrix material can be identified as well. The oxidation quantities for different samples with varying processing times are shown in figure 7. The intensities and the number of repetitions are adjusted to keep the ablation depth of the samples constant at  $41 \mu\text{m}$ . It is shown, that lower intensities and longer processing times lead to less oxidation of the carbon fibers. This shows the correlation between the intensities and the process temperature. The best value of  $2.42 \%$  Oxide for the shortest process time is carried out with an intensity of  $0.48 \text{ W/cm}^2$  and a scan-velocity of  $2 \text{ mm/s}$ . The highest achievable ablation rate for this parameter set is  $0.59 \text{ mm}^3/\text{s}$ .

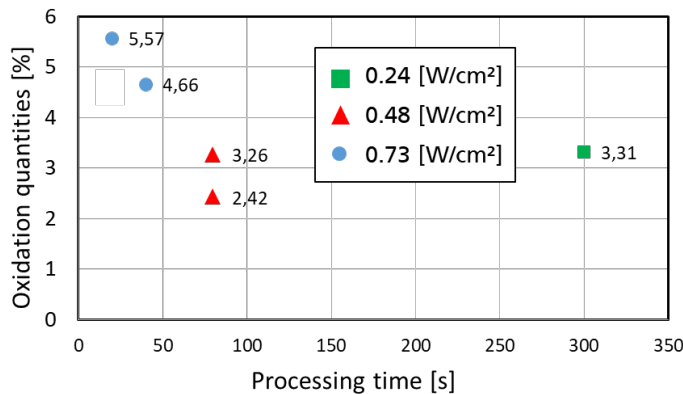


Fig. 7. Oxidation quantities of the carbon fibers at different processing times and intensities. The measurement is carried out by XPS analyses.

Comparing these values to the theoretical value after the graphitization process of about  $1 \%$  of volume fraction, an oxidation growth is recognized, which depends mainly on the applied intensities and the scan-velocity. Due to that, a small decrease of elasticity after the surface treatment must be taken into account. Nevertheless, almost all values of oxidation quantity stay below the  $5 \%$  which is achieved after the carbonization process (Cherif, C., 2011). Therefore, ablating the surface matrix material by the excimer laser



system is still of interest for sensor integration. An ablation of just the matrix material without exposing the carbon fibers for shimming process can also be achieved.

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