“Combined Plasma Laser Removal of Parylene Coatings”

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Abstract: The paper deals with the combination of atmospheric pressure plasma jet with ArF excimer laser for ablation of Parylene coatings. The main disadvantage of single laser treatment is debris produced during the laser ablation. Simultaneous supply of atmospheric plasma jet and laser beam reduces the debris considerably. The plasma jet obviates settling and cleans the fragments of polymer disintegration instantly at the appearance.

Keywords: Laser ablation, non-thermal plasma, plasma jet, parylene, coating

1. Introduction
This paper deals with the results of the simultaneous laser-plasma-treatment of Parylene-coatings. Parylene is the trade name for a variety of polyxylylene polymers. Parylene conformal coatings are ultra-thin, pinhole-free polymer coatings that find wide ranging application in medical devices, electronics, automotive, military, and aerospace industries. The family of Parylene coatings offer many valuable surface treatment properties to these industries, including excellent moisture, chemical, and dielectric barrier properties. Additionally, Parylene coatings offer thermal and UV stability, and dry-film lubricity [1].

For different reasons the coating has to be removed at certain places, for example to contact electrical circuit boards. It is very difficult to generate such areas by masks during the coating process. Those masks are wearing fast. Abrasive methods are also inapplicable; therefore the better alternative is to ablate locally the Parylene coating by laser radiation. But in this technology are some problems, too: The wavelength of the radiation has to be in the ultra violet, because the light absorption of Parylene increases for wavelengths shorter than 300 nm [2]. Also high fluences are needed. The high photon energy is needed to fragment the Parylene photo chemically into its chemical compounds - hydrocarbon fragments, carbon and its bonds. This carbon-particulate matter deposits as a black to brown inhomogeneous film in and around the ablated areas. This debris problem is unwanted in many applications, for example laser scanning processes. If it is necessary to ablate structures or areas which are greater than the laser spot size, the debris prevents reproduction in a good quality, because of the inhomogeneous absorption coefficient [3]. There are some examples for the usage of UV laser radiation for the removal of Parylene coatings in medical applications: recessing of planar stimulating electrodes or exposure of insulated microelectrodes [4],[5].

2. Experimental set-up
The following sections explain the experimental setup for hybrid laser plasma treatment and its components, the specimens which were used, and process parameters.

2.1 Specimens
The specimens are 0.5 mm thin steel plates coated with Parylene. The film thickness is approximately 5 µm. Parylene C belongs to the group of polyxylylene polymers. The chemical structure is shown in Fig. 1 [6].

![Fig. 1: Chemical structure of Parylene C](image)

The ablation threshold value of Parylene at 193 nm laser wavelength is given in the literature with 0.9 J/cm² [2]. With Parylene C coated soda-lime glass slides were used for measurement of light transmission. The relative transmission in range of 200 nm till 500 nm was measured by spectrometer and is shown in Fig. 2.

![Fig. 2: Relative transmission of Parylene C](image)

The transmission of UV light is for wavelength under 280 nm smaller than 0.03 %. The theoretical value of the reflection for Parylene C in the range of the visible light is calculated from the refraction index n = 1.639 to about 6%.
2.2 Plasma and laser sources
The plasma source which was used is the commercial plasma jet “Plasma-BLASTER” of the company “Tigres Dr. Gerstenberg GmbH”, Rellingen, Germany. According to the function principle of a jet (to blow out the plasma filaments through a nozzle with a gas flow) the plasma source works with atmospheric pressure and the treatment-head is very flexible to handle many kinds of surface topologies. As process gases are air, nitrogen, oxygen, argon, and their mixtures possible. The system generates a non-thermal short-lived discharge [7]. The equipment consists of a power pack and a treatment-head in which the plasma is generated.

The electrical discharge is initiated between the internal pin-shaped electrode and the external cylinder-shaped or truncated cone-shaped outside electrode which acts as the nozzle. Both parts are from stainless steel and replaceable. The filaments and the afterglow plasma are brought out of the nozzle with a gas flow from 20-30 l/min. The leaving plasma is potential-free. The discharge is driven with a sine-shaped voltage of about 12 kV. The output power is regulated by an impedance matching of the frequency in the range from 18 kHz up to 50 kHz [8]. The laser which was used is a product of the company “Coherent”. The maximum pulse energy of the ArF laser is 400 mJ and the pulse duration is 20 ns.

2.3 Parameters
The laser repetition rate of 50 Hz was used. The laser spot was rectangular with the dimensions 500 x 200 μm². The movement speed was 300 μm/s and therefore the overlap was 97%. A gas mixture of 20% oxygen and 80% nitrogen was used as process gas. The distance between nozzle and specimen was app. 5 mm. The ablated areas are stripes with a width of 500 μm and a length of 20 mm.

3. Results
The best results were obtained with the plasma-addition and a laser fluence of about 1 J/cm² and 60 pulses. The number of pulses was achieved by processing the ablated area twice with an overlap by 97%. The nearer the fluence is at the ablation threshold value, the cleaner the ablated area is. But the processing twice over is necessary.

Without the plasma-addition a fluence of 1.2 J/cm² is needed at the same parameters. At lower fluences the ablation was incomplete.

3.1 Analysis by microscopy
To evaluate and show the quality and completeness of the ablation in a good way a light microscope was applied. The results by using only a laser is shown in figure 4, and figure 5 shows the combination of laser and plasma ablation.

![Fig. 4: 100-times magnified microscope picture of only by laser ablated area, fluence 1.2 J/cm²](image)

![Fig. 5: 100-times magnified microscope picture of by laser and plasma ablated area, fluence 1.0 J/cm²](image)

In a short period after the treatment, the ablated areas of both methods were steel-grey (Fig. 5, middle part). But after 24 hour storage in atmosphere the only with laser ablated area showed considerable traces of oxidation. The light micrographs (Fig. 4 and 5) were made after 5 days of storage and without plasma-addition there is a lot of oxidation on the steel surface (Fig. 4, middle part). A 100x magnification is sufficient to detect the black debris within the ablated area. Outside the ablated area along the edges there is a massive deposition of debris. Figure 6 shows the edge of ablation with a magnification of 500. In the upper area there is the Parylene coating to see and in the lower region the ablated area. On the Parylene coating debris is located, which density decreases with the distance to the edge. On the ablated area there is debris and also oxidation to see. 
Fig. 6: 500-times magnified microscope picture of the ablation edge, ablation only by laser.

Fig. 7 shows the ablation edge with the plasma-addition. Here is no debris to detect and the oxidation is very little after 5 days of storage in atmosphere.

3.2 Further analysis

Before this experiments were carried out, the effect of the plasma-jet on the Parylene was examined. The AFM images in Fig. 8 show that a plasma treatment of the Parylene causes an increase in roughness of the surface. The top left micrograph shows the surface before and the lower right micrograph the surface after the treatment. The values of roughness of the untreated surface is 111 nm and of the plasma treated surface 248 nm.

The increase of the roughness influences the properties of reflection. The graph in Fig. 9 shows the differences in direct reflection for treated and untreated Parylene coatings on glass slides over the wavelength in the range from 190 to 300 nm. There is an explicit decrease in reflection through the plasma treatment.

Fig. 7: 500-times magnified microscope picture of the ablation edge, ablation by laser combined with external plasma.

Fig. 8: AFM-Pictures of untreated (upper) and plasma treated (lower) surface of Parylene C.

4. Conclusion

In summary we can say that Parylene is generally good to be ablated with a wavelength of 193 nm. The best results are to be obtained with fluences short above the ablation threshold which causes the need of high repetition rates and low process velocity. The processes overall slow and it is necessary run the process at least twice to get a complete ablation with a minimised accumulation of debris and influence on the substrate. Without the simultaneous plasma treatment the debris accumulation is too big that an afterwards cleaning process is still needed. By using 193 nm there is much ionized oxygen near the ablation area produced. This reactive oxygen may be the possible reason for the oxidation on the steel surface. The laser heats up the surface which reacts immediately with the ionized oxygen. Therefore it is critical in industrial or medical use to use only laser ablation to remove locally Parylene coatings from circuit boards or medical devices. Mainly in the medical applications are complex alloys used and a photochemically or thermally induced change by laser radiation would be having serious outcomes. Through the deployment of external plasma the debris is removed completely and no closing cleaning process is needed. Also the added plasma decreases the needed fluence and therefore the laser induced stress on the substrate decreases, too. The decrease of the threshold value is caused by the increased surface roughness and the involved increased absorption within the coating. Further it is possible that the energy rich electrons of the plasma excite the molecules of the Parylene and therewith an increase of the absorption during the process is taking place.

The preservation of the substrate can additionally to the lower fluence be explained by the properties of the plasma jet. The plasma contains mainly of ionized nitrogen. Exitid oxygen fetches caused by high electronegativity electrons to reach the rare gas configuration. The lifetime of O and O-2-Ions is long and they still chemical unreactive. Therefore there is less reactive oxygen at the ablation area during the process and mainly the excited and ionized nitrogen.

The additional plasma treatment causes a higher technical complexity but for some application it should be essential.
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6. References


