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Plasma-Enhanced Laser Materials Processing

Christoph Gerhard, Wolfgang Viöl and Stephan Wieneke

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Abstract

In the last few years, the combination of laser irradiation with atmospheric pressure plasmas, also referred to as laser–plasma hybrid technology, turned out to be a powerful technique for different materials processing tasks. This chapter gives an overview on this novel approach. Two methods, simultaneous and sequential laser-plasma processing, are covered. In the first case, both the plasma and the laser irradiation are applied to the substrate at the same time. Depending on the process gas and the discharge type, the plasma provides a number of species that can contribute to the laser process plasma-physically or plasma-chemically. Sequential plasma-enhanced laser processing is based on a plasma-induced modification of essential material properties, thus improving the coupling of laser energy into the material during subsequent laser ablation. Simultaneous plasma-assisted laser processing allows increasing the efficiency of a number of different laser applications such as cleaning, microstructuring, or annealing processes. Sequential plasma-assisted laser processing is a powerful method for the processing of transparent media due to a reduction in the laser ablation threshold and an increase in the ablation rate at the same time. In this chapter, the possibilities, underlying mechanisms, performance, and limits of the introduced approaches are presented in detail.

Keywords: Laser-plasma-hybrid techniques, atmospheric pressure plasma, cleaning, microstructuring, modification

1. Introduction

During the last decades, both lasers and plasmas have become essential integral parts of modern manufacturing technology and surface engineering. The coupling of laser irradiation and plasmas, which can be realized either at low or atmospheric pressure, has turned out to be a powerful combination for a number of different applications. For example, plasma-assisted pulsed laser deposition (PLD), which is performed in vacuum environment, allows

the generation of special functional thin films [1,2]. In this context, laser–plasma coupling also offers the possibility of increasing the total efficiency of PLD processes by a reduction of the laser ablation threshold of some target materials such as tungsten due to the plasma perforation of the target surface and a subsequent laser-induced bursting of gas-filled pores [3].

Plasma-enhanced laser materials processing at atmospheric pressure is most commonly known from welding technology. Here, the laser-induced plasma results in the formation of a so-called keyhole, which allows an improved stirring of the molten material as well as a significant increase in welding depth and thus a larger and more homogenous welding seam [4,5]. In this context, laser irradiation can also be added to plasma arc welding processes in order to improve the process performances [6,7]. The plasmas used for this purpose are usually high-energetic arc discharges, driven at several amperes, where the metallic work piece itself acts as counter electrode. However, these techniques are not suitable for the machining of temperature-sensitive materials or for obtaining marginal and locally well-defined material removal as required in the case of cleaning or microstructuring.

For the latter task, the so-called laser-induced plasma-assisted ablation (LIPAA) method represents a promising approach for plasma-enhanced laser materials processing. LIPAA was developed in order to overcome the limits during laser ablation of glasses which are given by the high transparency of such media. Here, a focused laser beam is guided through the glass work piece onto a metallic target which is placed close to the rear side of the glass. As a result, a laser-induced plasma is ignited within the gap between the work piece and the target. Ablation of the transparent glass is then obtained due to a successive deposition of an absorbing metallic layer on its surface and a charge exchange amongst ions and electrons as well as a transfer of kinetic or potential energy, provided by radicals and ions [8,9].

In the last years, the simultaneous or sequential combination of low-energetic atmospheric pressure plasmas, mainly based on dielectric barrier discharges (DBD) and thus featuring low gas temperatures, and laser irradiation has turned out to be a powerful tool for a number of different applications. Such combination is also referred to as laser–plasma hybrid technology and represents another approach for improving laser-based materials processing techniques such as modification, cleaning, drilling, and cutting as well as structuring. In this context, auxiliary plasmas allow to increase the total process and energy efficiency and to improve the machining quality as presented in more detail in this chapter.

2. Laser–plasma coupling

The aim of plasma-enhanced laser materials processing is to benefit from interactions and synergies arising from the particular phenomena provided by laser irradiation and plasmas in order to improve the machining efficiency and quality of different processes. As shown in Figure 1, this technology is based on either simultaneous or subsequent coupling of both energy sources and the resulting impact on any work piece surface.

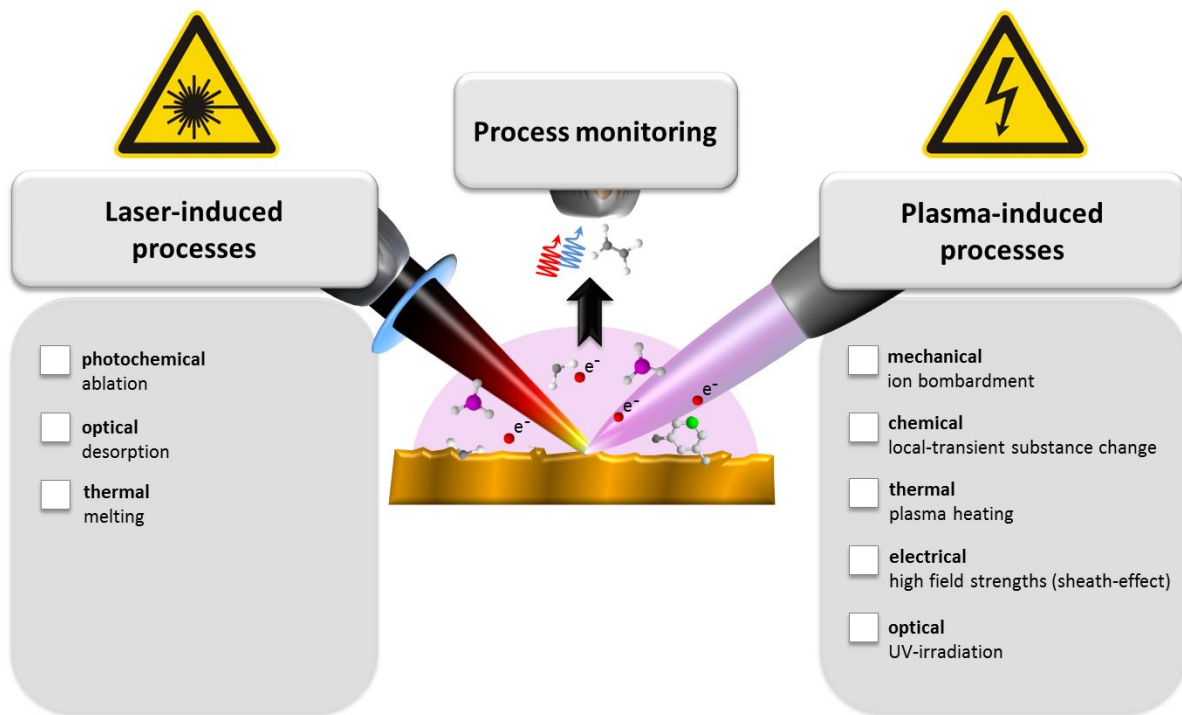


Figure 1. Schematic diagram of a hybrid laser–plasma machining process including particularly usable effects and mechanism.

Especially in the case of simultaneous processing, this approach results in a complex matrix laser-plasma-substrate. Thus, a proper inline process monitoring, for example, laser-induced breakdown spectroscopy (LIBS) or Rayleigh scattering analysis becomes crucial for a description and control of the process. This is of significant importance due to the number of different interacting parameters and mechanisms provided by laser irradiation and plasmas, which are introduced in more detail in the following sections.

2.1. Laser–matter interactions

Only three years after the presentation of the first operable laser source, its suitability for materials processing applications was demonstrated by the fabrication of diaphragms with an inner diameter of some microns [10]. Since that time, the laser has established as a state-of-the-art technology in different fields of materials processing and mainly material removal, commonly referred to as laser ablation. However, laser materials processing involves a number of different mechanisms such as photochemical, optical, and/or thermal processes, namely, ablation, desorption, or melting. Here, the particular process is set by the applied laser parameters.

The main influencing parameter during laser ablation is the wavelength-dependent absorption coefficient $\alpha(\lambda)$ of the particular substrate material, which determines the optical penetration depth of incoming laser irradiation with a certain wavelength λ . This material-specific property is given by

$$\alpha(\lambda) = \frac{4\pi k(\lambda)n(\lambda)}{\lambda} \quad (1)$$

with $k(\lambda)$ being the imaginary part of the complex index of refraction, i.e., the extinction coefficient, and $n(\lambda)$ being its real part, usually referred to as the refractive index. The optical penetration depth $d_p(\lambda)$ is then given by the reciprocal of the absorption coefficient according to

$$d_p(\lambda) = \frac{1}{\alpha(\lambda)} \quad (2)$$

It can easily be seen that surface absorption results from high absorption coefficients, whereas bulk absorption occurs in the case of low absorption coefficients. This fact is crucial for the choice of the laser wavelength for machining a given material with specific optical properties.

Another essential parameter for materials processing is the laser pulse duration τ . In the case of nanosecond laser ablation, material removal is mainly achieved by laser-induced heating and the subsequent desorption or melting and evaporation of material. Picosecond laser processing is based on the depletion of electrons, giving rise to a fast ionization within the substrate material, and thus resulting in material removal by Coulomb explosion due to the occurring repulsive forces of the remaining ions. Femtosecond laser machining processes are dominated by nonlinear effects induced by such ultrashort laser pulses such as temporally limited modifications in absorption within the processed material. Long-pulse and short-pulse laser materials processing are classified by the comparison of the optical penetration depth d_p (see Eq. (2)) and the thermal penetration depth d_{th} of laser irradiation. According to

$$d_{th} \approx \sqrt{2K\tau}, \quad (3)$$

the latter results from both thermodynamic material characteristics, expressed by the thermal conductivity K , and the laser pulse duration [11,12]. In the case of $d_p < d_{th}$, laser machining is referred to as long-pulse processing. In contrast, short-pulse processing is on hand when $d_p > d_{th}$.

The laser wavelength and its pulse duration further determine the laser fluence Φ (i.e., laser pulse energy E per illuminated area A) required for removing a given material. This parameter can also be expressed as dose D , given by the product of the laser pulse energy and the number of the applied laser pulses. Due to the thermal relaxation characteristics of solids, the laser pulse repetition rate f_{rep} finally has a considerable impact on multiple pulse laser machining processes given the fact that the average laser power P_{av} results from

$$P_{av} = Ef_{rep}. \quad (4)$$

To summarize, a number of different laser parameters have to be controlled in order to realize an optimized and high-quality machining process, depending on specific optical and thermodynamic characteristics of the work piece material. These laser parameters are wavelength, pulse duration, energy, and fluence as well as the repetition rate. In terms of plasma-enhanced laser materials processing, plasma–matter interactions have to be considered additionally.

2.2. Plasma–matter interactions

Similar to lasers, plasma sources have been used in manufacturing for several decades now, for example, for plasma cutting, arc welding, surface activation, or EUV lithography. This wide range of clearly different applications can be addressed, thanks to the versatility of technical plasmas. Plasma effects are generally influenced by the particularly applied operating parameters such as the high-voltage U , the high-voltage pulse frequency f , the composition of the process gas, the working distance, and the discharge type (direct or indirect). Due to this multiplicity of possible parameters and the resulting plasma–matter interactions, plasma technology is indeed a rapidly growing area of application but still represents a complex field of research.

Within a plasma volume, both neutral and charging electron collision-induced gas phase processes such as dissociation, excitation, ionization, and attachment can take place as visualized in Figure 2.

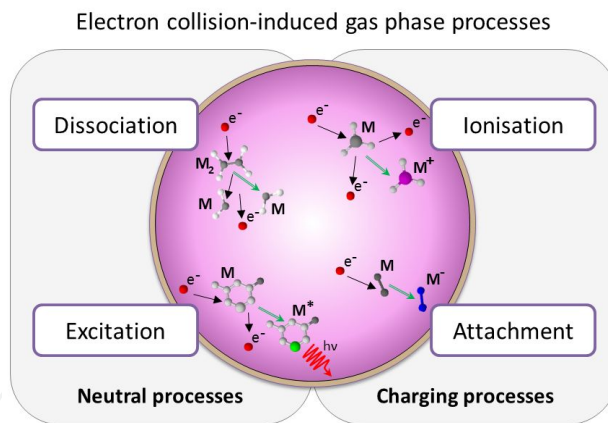


Figure 2. Schematic visualization of electron collision-induced gas phase processes in plasma bulks.

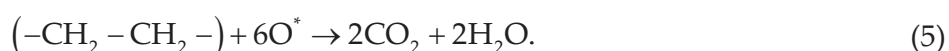
In terms of materials processing, plasmas thus potentially allow the following:

- The chemical reduction or oxidation of the work piece surface or adherents by chemically active plasma species (applicable for both direct and indirect discharges)
- An energy transfer to the work piece surface resulting from the de-excitation of metastable plasma species at walls (applicable for both direct and indirect discharges)
- A certain plasma heating of the work piece surface (applicable for both direct and indirect discharges)

- An acceleration of charge carriers due to a high electrical field strength in the sheath region on the work piece surface (applicable for direct discharges)
- The formation of UV radiation (applicable for direct discharges where UV radiation is generated close to the surface)

As listed above, some of these phenomena especially become of importance in direct plasma discharges where the work piece itself represents a component of the discharge geometry. The choice of the discharge type thus plays an essential role for any plasma-based materials processing application.

Plasma treatment is a state-of-the-art method for surface activation, mainly for improving the adhesion of lacquers or glues on synthetic materials by the formation of polar groups on the substrate surface [13,14]. Another established field of application is plasma sterilization [15] or plasma cleaning [16,17]. For the latter application, hydrocarbons ($-CH_2-$) represent the main surface pollutants. These pollutants can easily be removed by reactive oxygen species (ROS) such as atomic oxygen (O^*), provided by air plasmas, according to



However, an excitation of a carbon atom can also be achieved by collisions with electrons within the plasma as shown in Figure 3.

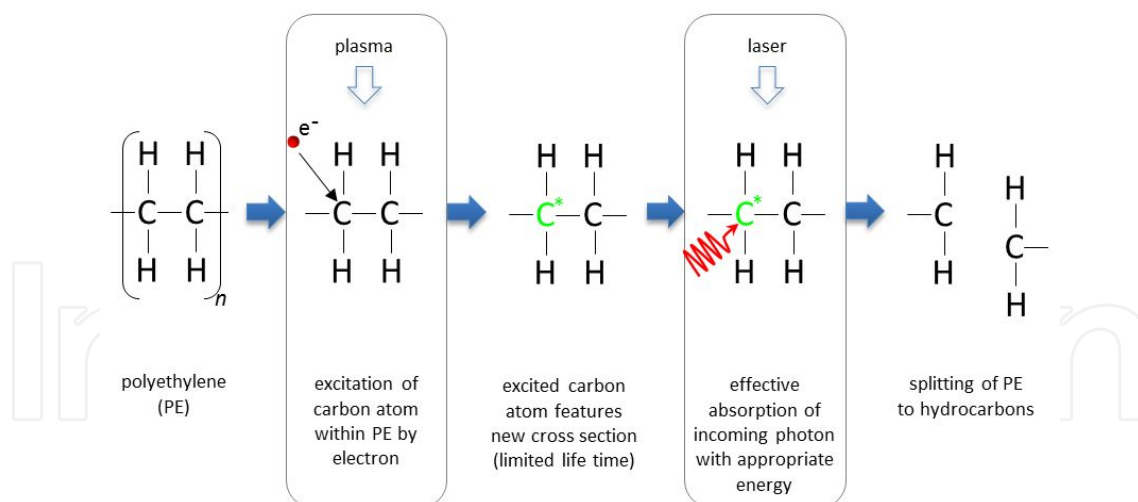


Figure 3. Splitting of polyethylene to hydrocarbons by electron-induced excitation of carbon atoms and subsequent absorption of incoming laser irradiation.

The carbon–hydrogen (C–H) bond features an original binding energy of approximately 4.4eV. Relating to laser irradiation, this energy corresponds to a laser wavelength of approximately 282 nm. Once a carbon atom within this bond is excited by such a collision, the energy required for breaking this bond is $<4.4\text{eV}$. The excitation of atoms by plasma thus offers new possibilities

for laser processes and especially allows the use of energy- and cost-efficient standard laser sources. In the example given above, a 3rd-harmonic Nd:YAG laser instead of a 4th-harmonic one could be used for material removal, consequently improving the total energy efficiency of such a laser-based process.

Due to the possibility of generating reactive species, plasmas are further suitable for surface etching [18]. For instance, silicon-based materials such as silicon dioxide (SiO_2) can be processed using fluorochemical compounds as process gas. According to



etching is achieved by chemical reactions of both fluorine (F) provided by the plasma and silicon dioxide. As a result, gaseous silicon tetrafluoride (SiF_4) and gaseous dioxygen (O_2) are formed. Such plasma etching is also referred to as reactive atomic plasma technology (RAPT®).

3. Plasma-enhanced laser processes

3.1. Simultaneous laser–plasma processing

For simultaneous laser–plasma processing, suitable plasma and laser irradiation are applied to the work piece at the same time in order to generate synergetic effects between both sources of energy. Since plasma-induced chemical reactions require a certain length of time that is typically much longer than the temporal distance between the single pulses of pulsed laser irradiation (e.g., 100 μs for a laser pulse repetition rate of 1 kHz), this approach is rather based on the utilization of plasma-physical effects as also listed in the inset in Figure 1. Here, the plasma discharge type plays a key role since some of these effects are only existent in either direct discharges or remote plasmas. In addition, plasma-chemical effects such as a constant chemical reduction or oxidation can contribute to the process as for example, in the case of laser–plasma cleaning.

3.1.1. Laser–plasma cleaning

Plasma-enhanced laser processing is suitable for cleaning contaminated and oxidized or corroded surfaces and can also be applied for the removal of coatings or lacquers. In the first case, the actual laser cleaning process, based on desorption or ablation of surface-adherent contaminants, is supported by a modification of such contaminants by suitable plasmas. Depending on the chemical composition of the contaminants, either chemically reducing or oxidizing plasmas are applied. As an example, the reduction of surface-adherent oxides is achieved by the use of nitrogenous or hydrogenous process gases, whereas oxygen plays a key role for the removal of carbon-based layers (compare Eq. 5). Employing both laser and plasma cleaning at the same time allows a significant increase in cleaning efficiency as exemplified in Figure 4.

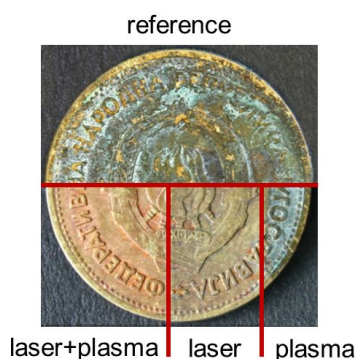


Figure 4. Photograph of a corroded coin (top) including plasma-cleaned (bottom right), laser-cleaned (bottom middle), and plasma-assisted laser-cleaned (bottom left) area

Here, laser–plasma cleaning of corroded coins was performed by introducing a plasma jet to Nd:YAG laser irradiation with a wavelength of 1064 nm. The plasma process gas was a mixture of argon (95%, carrier gas) and hydrogen (5%), leading to the formation of hydrogen radicals within the plasma [19,20]. Even though a pure plasma treatment features only a marginal cleaning efficiency, the combination of both laser-induced cleaning and plasma-induced reduction is a powerful tool for this task. In addition to an improvement of the cleaning efficiency, this hybrid approach also allows to reduce the laser fluence required for the cleaning process. In the present case shown in Figure 4, the laser fluence for cleaning was 0.6 J/cm² without any plasma and 0.4 J/cm² when applying the plasma simultaneously [19]. Thus, the required laser fluence is reduced by a factor of 1.5, which notably contributes to the overall energy efficiency of such hybrid cleaning processes.

As shown by Eq. 5 and illustrated in more detail in Figure 3, both plasma-chemical and plasma-physical processes can furthermore contribute to the laser removal of carbon-based coating materials such as parylene [21] by the excitation of carbon bonds or the oxidation of hydrocarbons. For this purpose, air can be used as process gas. Based on these effects, laser–plasma cleaning is thus a suitable technique for an efficient removal of graffiti sprays, spray lacquers, acryl paints, and acrylic and alkyd resins [22]. Since laser-based processes can be performed localized with a high accuracy, laser–plasma cleaning is thus of interest for the selective removal of protecting layers, e.g., for electrical contacting, the large-scale removal of bleached and aged lacquers, the restoration of artworks, etc.

3.1.2. Laser–plasma annealing

For the production of thin film transistor (TFT)-based flat screen displays, excimer laser annealing (ELA) represents an established method. Here, large-scale crystallization of amorphous silicon layers on glass substrates is performed by specifically shaped, i.e., laterally homogeneously distributed laser beams [23]. The efficiency of this technique is currently limited by the laser energy of available sources. In order to overcome this restriction and to machine a large surface area, several excimer laser sources are coupled in order to achieve energy densities sufficient for large-scale annealing. In this context, adding appropriate plasma

sources to the ELA process allows an increase in the process efficiency. Such increase can be achieved by simple plasma-induced heating of the silicon layer, which directly impacts the temperature-dependent band gap $E_g(T)$ as expressed by the Varshni equation [24], given by

$$E_g(T) = E_g(T = 0K) - \frac{\alpha T_{\max}^2}{T_{\max} + \beta}. \quad (7)$$

Here, α , β , and $E_g(T = 0K)$ are material constants.

Another approach is to add cold, physically active plasmas to an ELA process. For example, direct DBD argon plasmas turned out to be suitable for increasing the crystallization efficiency by a factor of maximum 1.9 [25] as exemplified in Figure 5.

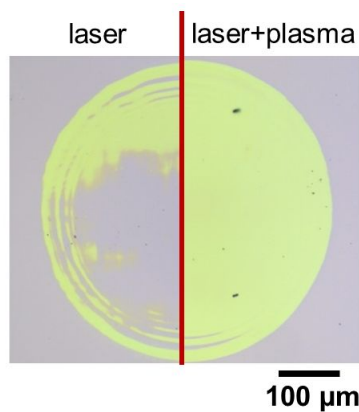


Figure 5. Microscopy image of silicon layer after pure excimer laser annealing (left) and plasma-assisted excimer laser annealing (right).

Even though the underlying mechanisms of this approach are not yet fully understood, the increase in crystallization efficiency is most likely due to a plasma-induced additional energy transfer by inelastic collisions of excited argon atoms and metastable argon species at the silicon layer surface as described in more detail in Section 3.1.4. Further, the formation of dipoles within the amorphous silicon layer due to the used direct discharge and the accompanying change in optical properties can contribute to an improved coupling of incoming laser energy into the layer. Even though laser–plasma annealing allows a significant enhancement of an ELA process in terms of its efficiency, it is subject to the restriction that the silicon-coated substrate necessarily has to be brought into a direct DBD plasma. The application of this method on an industrial scale, where typically laser line foci with a width of 1 to 1.5 m are used for ELA, is thus a challenging task to be solved in the future.

3.1.3. Laser–plasma engraving

Laser engraving is applied for the realization of microstructures for micromechanical devices and actuators or for marking print rolls. Here, the most disturbing effect is the formation of

burrs and debris, i.e., resolidified material and condensed material vapor close to the ablation area. Typically, such burrs and debris droplets are of the same size as the actual laser-engraved structure and consequently limit the performance of any microstructured functional device. The use of assisting plasmas during laser engraving allows a reduction of these effects. As confirmed by X-ray photoelectron spectroscopic analysis of laser-induced debris on stainless steel, it is chemically reduced when applying appropriate plasma process gases. As a result, the debris features notably lower content of oxygen [26]. The additional (thermal) energy provided by the plasma further gives rise to a higher degree of vaporization of the laser-induced plume and thus inhibits the recondensation of material on the surface as shown by the comparison in Figure 6.

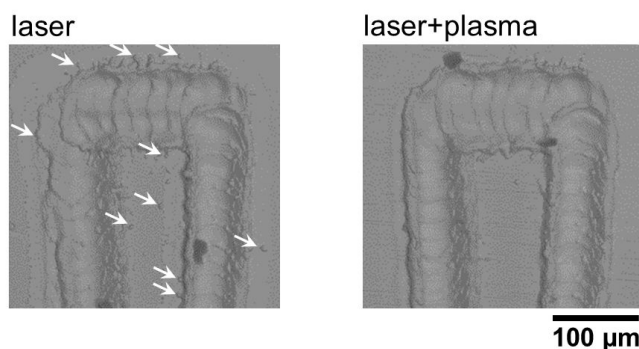


Figure 6. Scanning electron microscopy image of microstructures on stainless steel realized by pure (left) and plasma-assisted (right) laser engraving, considerable debris droplets are indicated by white arrows.

In principle, the formation of debris during laser engraving of different metals and alloys can be reduced by assisting plasmas [26]. However, this effect is strongly dependent on the particular chemical composition of the work piece and the plasma process gas mixture.

3.1.4. Laser–plasma drilling and cutting

Simultaneous plasma-enhanced laser processing can be applied for increasing the ablation rate during laser machining of various materials. As a consequence, the efficiency of laser drilling and cutting can be improved. For this purpose, a direct DBD-based argon plasma beam can be introduced to a focused laser beam, where both the plasma beam and the laser beam are guided coaxially as presented in more detail in [25,27–29]. As shown in Figure 7, this configuration allows increasing the ablation depth during laser drilling of optical glasses by a factor of approximately 2 in comparison to pure laser drilling without any assisting plasma [27].

It can also be applied to metals, where the maximum increase in volume ablation rate was even reported to be by a factor of 9.6 in the case of aluminum [28]. Principally, an increase in ablation rate was also achieved for aluminum oxide [29]. As observed by laser-induced breakdown spectroscopic measurements during both pure laser ablation and simultaneous plasma-assisted laser ablation of aluminum oxide, applying plasma additionally results in an intensification of characteristic spectral lines of aluminum ions (AlII) as shown in Figure 8.

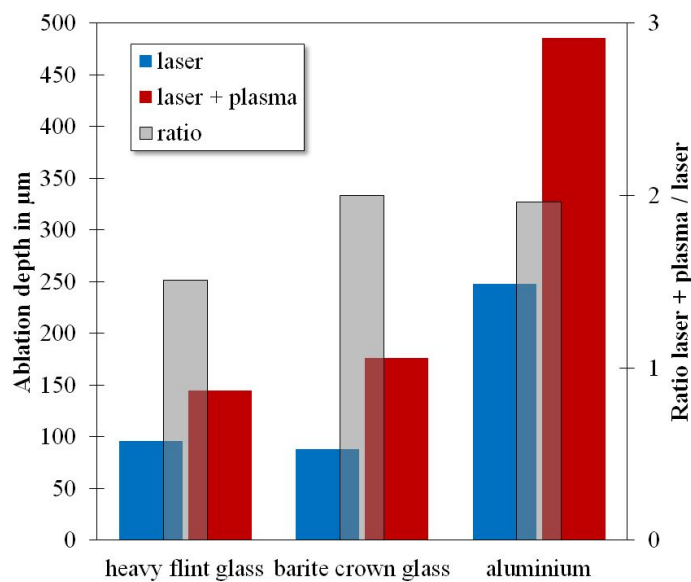


Figure 7. Comparison of the particular laser ablation depths of heavy flint glass, barite crown glass and aluminium obtained by 40 laser pulses at a fluence of 404.6 J/cm² without (blue columns) and with (red columns) assisting plasma including particular ratios (gray columns).

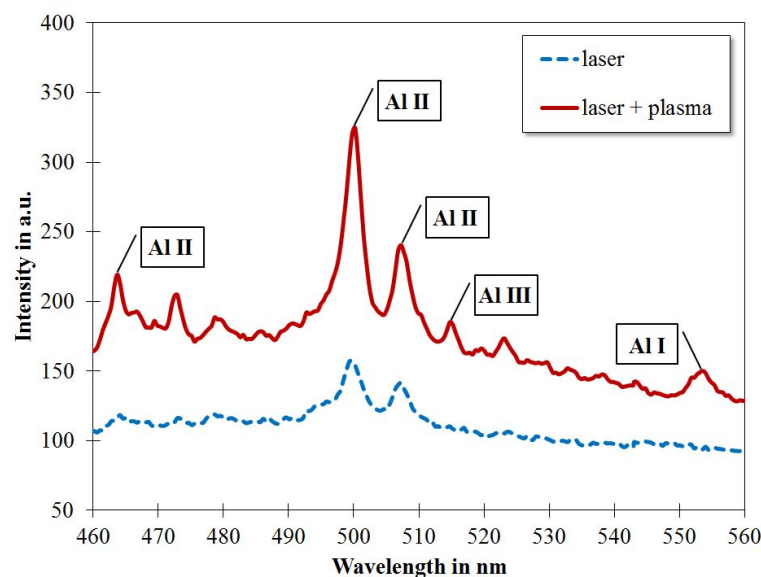


Figure 8. Optical emission spectra taken during pure laser ablation (blue dashed line) and plasma-assisted laser ablation (red solid line) of aluminum oxide ceramic.

Further, more spectral lines of neutral aluminum (AlII) and aluminum ions (AlII and AlIII) appear. This confirms the increase in material removal by a plasma-induced high-energetic process with respect to pure laser machining. However, this increase cannot be explained by a simple addition of the particular energies of the laser and the plasma. It is rather a synergetic effect, which can be described as follows: In the course of the laser evaporation process, the particles within the arising laser plume feature a considerably large surface for collision

processes. Such collision results in a de-excitation of excited plasma species [30] and thus comes along with the disposal of energy, which amounts to 11.55 eV for the 3P_2 argon metastable (Ar^m) state and 11.72 eV for the 3P_0 Ar^m state, respectively. The formation of an ablation plume by the laser is thus of significant importance for energetic laser–plasma synergies that arise from this mechanism.

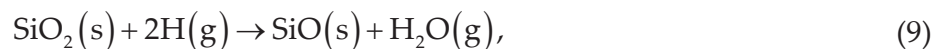
Since in the above-described setup, the work piece is placed within the discharge gap, the coupling of incoming laser energy can furthermore be supported by local-transient substance changes as, for example, a formation of dipoles and the accompanying modification of near-surface optical properties. Another—although marginal—effect during simultaneous plasma-enhanced laser machining is the influence of the plasma beam on the propagation characteristics of the laser beam. Here, the plasma acts as thermal gradient index lens, thus resulting in a certain focus shift of the passing focused laser beam. However, due to the relatively low gas temperature of DBD plasmas, this focus shift of 2 to 4 mm [31] is usually much lower than the Rayleigh length z_R of the focused laser beam which is given by

$$z_R = \frac{\pi w_0^2}{\lambda}. \quad (8)$$

For instance, z_R amounts to approximately 31.5 mm for a focused fundamental Nd:YAG laser beam with a beam waist radius w_0 of 100 μm , which is approximately 8-fold the focus shift induced by the plasma beam. This effect thus turns out to have a marginal influence during plasma-assisted laser drilling but may become of importance in the case of surface micro-structuring applications.

3.2. Sequential laser–plasma processing

Sequential laser–plasma processing represents a powerful tool for enhancing the laser machining quality and efficiency of transparent media such as glasses. This method is a combination of plasma pretreatment and subsequent laser ablation. Using hydrogenous process gases for plasma pretreatment, the energy coupling of incoming laser irradiation can be significantly improved due to a modification of the optical properties of the work piece. First, the process gas is dissociated as a result of collisions with electrons within the plasma volume. The atomic hydrogen generated in this vein can then induce several reactions at the surface of the work piece. In the case of glasses, the main mechanisms are the chemical reduction of glass network-forming oxides such as silicon dioxide (SiO_2) according to



resulting in the formation of a substoichiometric mixed phase at the surface, and the implantation of hydrogen into deeper regions of the glass bulk material. The substoichiometric mixed phase can be referred to as silicon suboxide (SiO_x , where $1 < x < 2$). Due to the comparatively

low penetration depth of plasma-chemical reactions, the thickness of this reduced layer amounts to approximately 100 nm [32]. Silicon suboxide is dominated by oxygen deficiencies and E' centers, which represent optically active defects and give rise to an increase in absorption in the wavelength range from 177 to 218 nm [33]. Moreover, the hydrogen implanted by the plasma induces a hydrolytic scission of the glass network, resulting in the formation of non-bridging oxygen (NBO) and H(I)-centers up to a penetration depth of several microns. These defects generate an increased absorption between 206 and 258 nm [33]. As shown in Figure 9, both effects (and further interacting phenomena such as a certain surface wrinkling [34]) result in a considerable increase in UV-absorption, depending on the plasma treatment duration.

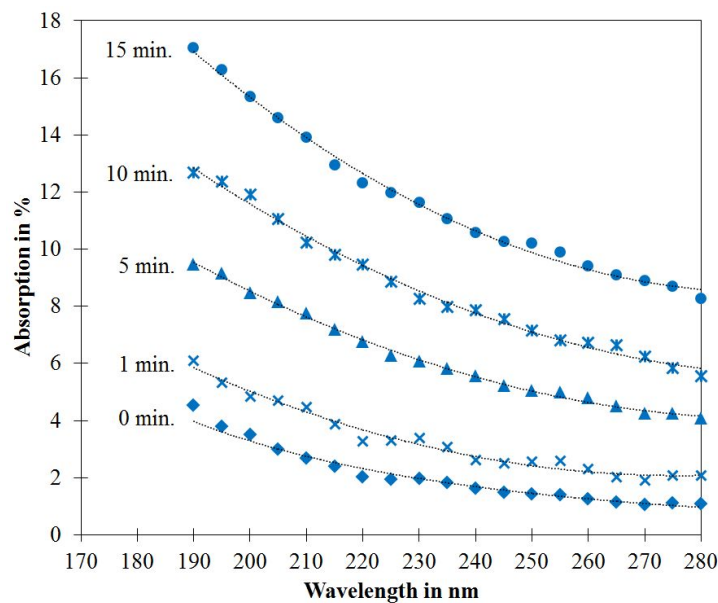


Figure 9. Absorption spectra of 5 mm thick fused silica before (0 minutes) and after plasma treatment for 1, 5, 10, and 15 minutes, respectively.

One has to notice that this increase in absorption is a reversible process. The initial transmission characteristics can nearly be reobtained by tempering the plasma-treated glass and thus removing the implanted hydrogen and reoxidizing the glass network [35].

In terms of laser ablation subsequent to the plasma pretreatment, the increase in absorption allows a notable reduction of the laser ablation threshold up to a factor of 4.6 when using an argon-fluoride excimer laser with an emission wavelength of 193 nm [36]. Due to the accompanying decrease in energy deposition into the glass, a higher contour accuracy and lower roughness of the ablated area is achieved as exemplified in Figure 10.

Thus, the sequential laser-plasma processing of glasses allows both a saving of laser energy and an improvement of the machining quality at the same time [37]. The implanted hydrogen further acts as reaction partner for oxygen within the SiO₂ network during multiple pulse laser ablation. This results in the formation of a new substoichiometric layer at the bottom of the ablated area as confirmed by secondary ion mass spectroscopic investigations. As a result of

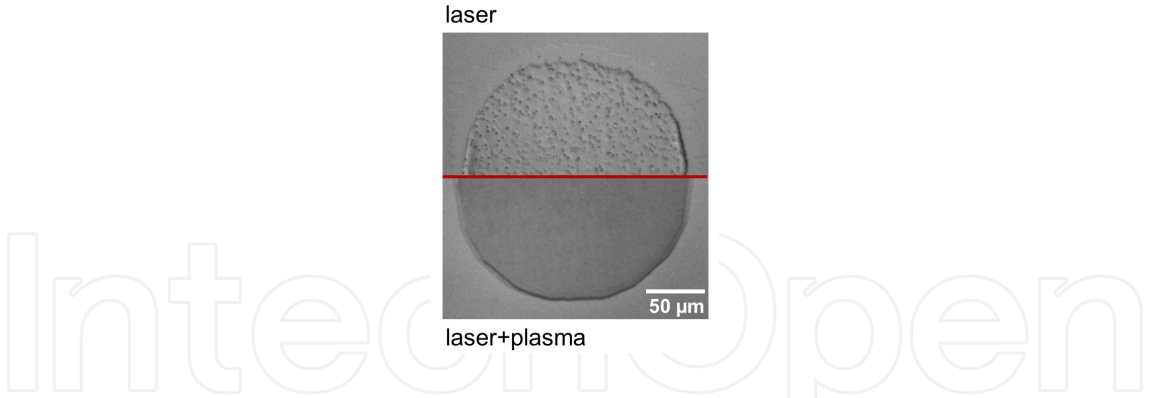


Figure 10. Microscopy image of single-pulse laser ablated spots on fused silica without (top) and with (bottom) plasma pretreatment, each ablated at the particular ablation threshold of 6 J/cm² (top) and 1.3 J/cm² (bottom), respectively.

this laser–plasma-induced effect, the absorption for each following laser pulse and consequently the depth ablation rate is constantly increased with respect to pure laser ablation as shown in Figure 11 [38].

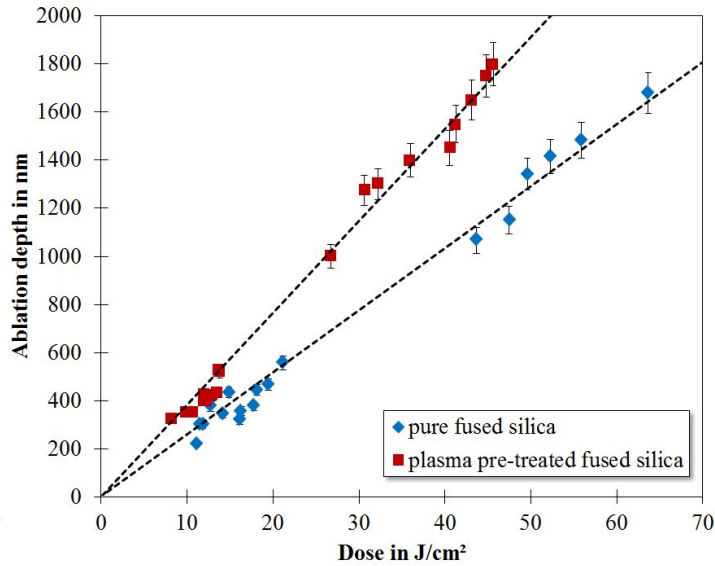


Figure 11. Dose-dependent ablation depth of fused silica ablated by excimer laser irradiation without (blue rhombi) and with plasma pretreatment (red squares).

In addition to a decrease in ablation threshold, an increase in ablation rate and an improvement of the contour accuracy the above-described plasma treatment allows the use of energy-efficient laser sources. Due to the plasma-induced increase in UV absorption, 4th-harmonic Nd:YAG lasers instead of excimer lasers can be applied for machining fused silica [39]. Even though the highest efficiency of the plasma pretreatment is found in the case of fused silica as substrate material, this approach can also be successfully applied to optical glasses [40] or technical glasses such as photovoltaic cover glasses [41]. However, due to the significantly denser network of multi-component glasses, the implantation of hydrogen and the formation

of the above-described related mechanisms that come along with the presence of hydrogen are limited.

The above-described plasma pretreatment strongly influences the surface polarizability k_s and the molecule polarizability α_m of any substrate. According to the Clausius–Mosotti equation, given by

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N_A \rho \alpha_m}{3 \epsilon_0 M}, \quad (10)$$

where N_A is the Avogadro constant, ρ is the density, ϵ_0 is the vacuum permittivity, and M is the molar mass, α_m is directly related to the refractive index n [42]. Since the polarizability is increased and taking Snell's law into account, this leads to a refocusing of incoming focused laser irradiation and a more localized input of laser energy, respectively, coming along with an increased fluence close to the substrate surface. This effect further contributes to the above-described mechanisms in the case of sequential laser–plasma processing.

4. Summary

The combination of both atmospheric pressure plasmas and laser irradiation allows increasing the total process efficiency and machining quality of a number of laser-based processes such as cleaning, modification and material removal. For this purpose, either plasma-chemical or plasma-physical effects or mechanisms can be employed. Chemical plasma effects involve the reduction, oxidation, or excitation of bonds, which contribute to laser-induced removal of pollutants or layers. Plasma-physical effects such as collision-induced de-excitation of metastables and high electric field strengths at work piece surfaces can be used in order to improve the modification of coatings and to increase the laser ablation rate. Due to the multiplicity of laser and plasma parameters, the partial complexity of the underlying mechanisms and interactions and the wide range of different materials, plasma-enhanced laser materials processing is still at an early stage. However, the suitability of this approach for a number of different applications was shown over the last years as presented in this chapter. In order to implement this technique in an industrial scale where focused laser beams are usually scanned for large-scale treatment, appropriate and adapted plasma sources should be developed. Due to the principle of DBD plasma sources, such upscaling can be realized quite easily. To summarize, it can be stated that the coupling of laser irradiation and atmospheric pressure plasmas facilitates the valorization of a variety of laser processes based on cost- and energy-efficient nanosecond laser sources.

5. Nomenclature

A: area

D : laser dose

d_p : optical penetration depth

d_{th} : thermal penetration depth

E : laser pulse energy

$E_g(T)$: temperature-dependent band gap

f : high-voltage pulse frequency

f_{rep} : laser pulse repetition rate

K : thermal conductivity

$k(\lambda)$: wavelength-dependent extinction coefficient

k_s : surface polarizability

M : molar mass

N_A : Avogadro constant

$n(\lambda)$: wavelength-dependent refractive index

P_{av} : average laser power

U : high-voltage

w_0 : beam waist radius

z_R : Rayleigh length

α_m : molecule polarizability

$\alpha(\lambda)$: wavelength-dependent absorption coefficient

ϵ_0 : vacuum permittivity

λ : wavelength

ρ : density

τ : laser pulse duration

Φ : laser fluence

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Author details

Christoph Gerhard^{1*}, Wolfgang Viöl^{1,2} and Stephan Wieneke^{1,2}

*Address all correspondence to: christoph.gerhard@ist.fraunhofer.de

1 Application Center for Plasma and Photonics, Fraunhofer Institute for Surface Engineering and Thin Films, Göttingen, Germany

2 Laboratory of Laser and Plasma Technologies, University of Applied Sciences and Arts, Göttingen, Germany

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