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Introduction and Motivation

Nowadays, optical micro components and systems represent key devices for a number of daily-used convenience goods and apparatuses such as multimedia terminals, safety devices and medical equipment. For instance, micro lenses and optical systems are required for fibre couplers in telecommunication applications, CD and DVD players, micro cameras for safety monitoring or park assistance assemblies as well as endoscopes and fibrescopes in medical engineering. Besides, such devices have outstanding relevance for research and industry and contribute to the development of novel techniques and processes. In this context, micro lens arrays for laser beam shaping by optical homogenisers or micro optical monitoring systems for industrial vision, logistics planning and traffic management shall be mentioned exemplarily amongst a number of micro-optical, optoelectronic and opto-mechanical components and systems.

In this context, fused silica has become one of the most important materials in modern optical technology. This medium stands out due to a number of advantageous properties such as a low coefficient of thermal expansion, a high chemical resistance, a low dispersion and a high transmission in the ultraviolet (UV) wavelength range. However, the use of further optical glasses with differing indices of refraction and dispersion characteristics becomes crucial for the realisation of optical systems with high image quality and colour fidelity. As an example, the combination of both crown and flint glasses allows the correction of chromatic aberrations. The simplest example for such a combined optical system is an achromatic lens where chromatic correction is realised for two selected wavelengths.

For structuring and patterning optical glasses with structures in the range of some microns to some tens of microns, different techniques such as lithography or reactive ion etching can be applied. However, referring to complexly-shaped required surface forms, laser micro structuring is the preferable method. Here, UV lasers are usually used in order to overcome the high transmission and to benefit from the short laser wavelength for the realisation of (sub)micro structures. However, such techniques are partially limited due to the high required fluence for initialising ablation. In order to increase the coupling of laser energy into the highly-transmittive glass surface, hybrid laser ablation methods can be used. Here, absorbing layers are applied to the surface. Such techniques thus allow a significant decrease in the laser ablation threshold. However, the use of chemicals as well as time-consuming final cleaning procedures can become necessary in order to remove residues of the particularly used absorbing substance. In addition, comparatively low ablation rates are obtained by some of the existing techniques, resulting in poor process efficiency.

Against this background, novel hybrid laser ablation techniques for machining optical glasses are presented in the present work. These hybrid techniques are based on atmospheric pressure plasmas, which were introduced to classic laser ablation processes. This combination was chosen due to the fact that atmospheric pressure plasma sources feature a high efficiency, stability and reliability. Depending on the used process gas, a number of technically usable plasma properties such as a certain defined chemical, physical and electrical activity can furthermore be generated. Two different strategies, sequential and simultaneous plasma-assisted ablation, were investigated. Regarding sequential plasma-assisted ablation, the glass surfaces are pre-treated by chemically reactive hydrogenous atmospheric pressure plasmas before laser ablation. Such pretreatment allows a significant modification of the optical properties, giving rise to an increase in absorption. In contrast to existing hybrid ablation techniques, the absorbing layer is thus generated directly within the bulk material to be ablated. This effect is utilised in order to improve the energy coupling of incoming laser irradiation into the pretreated glass surface. In addition to this sequential process, a simultaneous plasma-assisted ablation method, based on a chemically inert process gas, is presented and discussed. Here, the laser ablation process is assisted by plasma-physical interactions. With respect to pure laser ablation, both investigated hybrid techniques allow a significant improvement of laser machining results and a considerable saving of laser energy. Owing to the adaptivity of the used plasma sources, the presented plasma-assisted ablation methods can easily be adapted to almost any existing industrial laser source by flanging the particular plasma nozzle.

Enhanced laser-based structuring of optical glasses is of notable interest for manufacturers of optical components and systems, laser micro machining facilities and users of such systems. The aim of the present work is thus to provide a description of novel approaches as well as an understanding of the underlying mechanisms for highly-efficient and versatile laser ablation methods for micro structuring of transparent silicon dioxide-based optical media.

2

State of the Art and Research

In this chapter, basic interactions and mechanisms of both atmospheric pressure plasmas and laser irradiation with glasses are described. First, an overview on established and lab-scale methods for atmospheric pressure plasma-induced etching, cleaning and activation as well as the particularly underlying mechanisms and effects is given. Second, the principles of laser interaction with glassy bulk material, laser ablation and the influence of the laser pulse duration on the ablation process are introduced. Finally, the most common hybrid methods for laser ablation of transparent media are presented.

2.1 Interactions of atmospheric pressure plasmas with glasses

Atmospheric pressure plasmas (APP) have achieved significant importance in a number of different fields of application. As the main advantage, no cost-intensive vacuum chamber and equipment, which would limit the dimension of work pieces, are required. This enables the integration of APP into large-scale industrial processes such as hybrid APP-assisted welding or joining. Owing to the low gas temperature of dielectric barrier discharge (DBD) plasmas, temperature-sensitive materials such as plastic sheets and lumbers [ben04] can be processed by this special type of APP. It is also suitable for the treatment of human tissue [mar12] for medical applications such as wound healing, disinfection [emm13] and microbial decontamination [ehl11]. Due to a comparatively low effective depth of action of approximately some tens to hundreds of nanometres, plasma processes are generally near-surface impacting. Depending on the plasma parameters, i.e. for example the plasma power, the process gas and, as the case may be, precursors, a number of different surface effects can be realised. Besides surface reduction, activation by the plasma-induced formation of functional groups [kog04] and wrinkling, surface oxidation and passivation [dah12] shall be mentioned. Such effects can be used in order to increase the surface adhesion of different substrates such as polymers [bel12] and glasses [shu12].

Atmospheric pressure plasma etching of glasses

In a number of applications such as micro-structuring of semiconductors, scribing integrated electric circuits by mask projection techniques and correction of micro-optics, reactive ion etching (RIE) techniques [lee99, nus97] are well-established production methods. For this dry etching process, the particular work pieces are placed within a vacuum chamber and exposed to a high-energy ion beam. However, direct plasma etching of glasses and glassy materials can also be achieved at atmospheric pressure by the use of reactive process gases and gas mixtures. Such methods are usually referred to as reactive atomic plasma technology (RAPT$^{®}$) and have recently gained in importance for precision machining applications such as etching of micro channels and structures or space-resolved asphERISATION and polishing of optically operative surfaces. In general, such techniques require the use of fluorochemical compounds (MF_x) as process gas as shown schematically in figure 2.1.

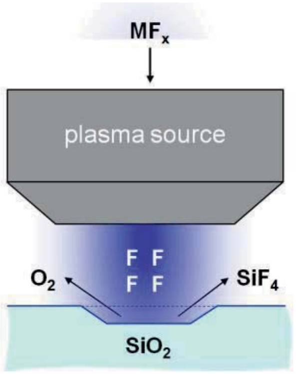

Fig. 2.1: Functional principle of reactive plasma etching

Here, etching is accomplished by chemical reactions of both fluorine (F) and silicon dioxide (SiO_2) to gaseous silicon tetrafluoride (SiF_4) and gaseous dioxygen (O_2) according to

$$SiO_2 + 4F \rightarrow SiF_4 + O_2. \tag{2.1}$$

In 1998, *Jeong* et al. reported on etching of fused silica using an atmospheric pressure plasma jet at room temperature (293 K). This rotation-symmetric jet source was driven by 13.56 MHz radio frequency (RF) at a power of 500 W. The used process gas was a mixture of helium (He [97%]), oxygen (O_2, [1%]) and tetrafluoromethane, a.k.a. carbon tetrafluoride (CF_4 [2%]), where the helium flow rate was 51 litres/minute (slm). The distance between the plasma jet nozzle outlet and the fused silica samples was 5 mm. Using this configuration, fused silica was etched at an etch rate R_{etch} of 1.5 µm/minute [jeo98].

Smoothing and precision correction of optical surfaces made of fused silica by an atmospheric pressure plasma jet source was introduced by *Schindler* et al. in 2005. Here, the plasma was microwave-excited with a microwave power of some hundreds of watts. In this case, reactive species were generated from the process gas, a composition of argon (Ar), sulfur hexafluoride (SF_6) and nitrogen (N_2). As a result, material removal was achieved by fluorine-induced reactions with fused silica and the formation of gaseous silicon tetrafluoride (SiF_4). Volume etch rates up to some 10 mm³/minute were obtained [sch05a].

Another etching process for fused silica applying an atmospheric-pressure pulsed remote plasma jet built up of two plane-plate electrodes was presented by *Iwasaki* et al. in 2006. The samples were placed 5 mm below the plasma jet nozzle outlet. As process gas, a mixture of Ar and CF_4 was used where the flow rates amounted to 0.24 slm for Ar and 0.06 slm in the case of CF_4. Experiments were performed for different plasma pulse repetition rates f_{rep} in the range from 5 to 20 kHz. It was shown that the etch rate was strongly depending on the pulse frequency where higher pulse frequencies resulted in higher etch rates with a maximum value of approximately 130 nm/minute at

$f_{rep} = 20$ kHz. When adding O_2 to the process gas, this value was increased up to 400 nm/minute whereas the addition of water vapour (H_2O) resulted in an even higher etch rate of 8 µm/minute. Based on the characterisation of the plasma volume that was performed by the use of ion attachment mass spectrometry (IAMS), this water-induced significant increase in ablation rate was considered to be due to the generation of hydrogen fluoride (HF) from CF_4 and H_2O [iwa06].

The dependency of the etch rate on the process gas composition during atmospheric pressure plasma etching of fused silica was also observed by *Oh* et al. in 2010. Experiments were performed using a remote plasma jet source based on a DBD. Here, the electrode configuration was a multiple pin-to-plate setup, driven by a frequency of 20 to 40 kHz at a plasma power of 4 kW. The considerations were mainly focussed on the influence of the process gas mixture, consisting of nitrogen (N_2 [30 to 80 slm]) and nitrogen trifluoride (NF_3 [0.2 to 1 slm]), on the resulting etch rate. Further, the impact of different additives, i.e. helium (He), Ar and O_2, each at a flow rate of 0.2 to 1 slm, was investigated. For this purpose, fused silica samples were placed on a motorised linear stage at a distance of 2 mm from the plasma source outlet. During the experiments, the sample traverse speed was 0.25 metres/minute. It was shown that the maximum etch rate was obtained for a medium flow rate of N_2 (60 slm) and a high NF_3 flow rate (1 slm) which was explained by the resulting high fluorine atomic density caused by the high plasma density within this given process gas composition. The addition of He and Ar effected a further increase in etch rate by an additional increase of the fluorine density as a consequence of *Penning* ionisation and dissociation processes[1]. Further, the etching process was amplified for higher pulse repetition rates. The maximum etch rate was found to amount to approximately 323 nm/scan at a traverse speed of 0.25 metres/minute [oh10].

Apart from fused silica, plasma etching at atmospheric pressure can also be achieved in the case of other glasses. Etching of Ultra Low Expansion (ULE®) glass from Corning, Inc. by applying an inductively coupled plasma (ICP) jet at atmospheric pressure with an effective area of approx. 314 mm² was presented in 2006 by *Fanara* et al. The plasma source was run at powers ranging from 1250 to 1500 W. The process carrier gas was Ar, which was nourished by NF_3 (10 to 20%). Here, a volume etch rate up to 0.55 mm^3/second was achieved. It was shown that the reactive gas concentration is rather of importance than the applied plasma power. Further, the etch rate is not influenced by thermo-chemical effects [fan06a].

A further interesting application of atmospheric pressure plasma sources in terms of the machining of glassy materials was presented by *Al-Shamma'a* et al. in 2002. Here, cutting of fibre glass mats with a thickness of 2 mm was achieved using an atmospheric microwave plasma jet. The microwave frequency was 2.45 GHz and the microwave power amounted to 3 kW. As process gas, Ar at a flow rate of 10 slm was applied. After cutting the samples at a traverse speed of 10 mm/second, no singeing of the cutting edges was observed [als02].

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[1] Basically, *Penning* ionisation describes an ionisation process resulting from the interaction of excited atoms or molecules and neutral molecules and atoms [pen27].

Atmospheric pressure plasma etching is also applied for other silicon-based materials that are commonly used in the manufacture of optical components of high precision. As an example, figuring and polishing of silicon carbide (SiC) with atmospheric pressure plasma jets using a process gas mixture containing CF_4 was reported by *Wang* et al. in 2006 [wan06] and *Arnold and Böhm* in 2012 [arn12]. Such technique was also applied in order to polish optical components made of pure silicon (Si) as presented by *Zhang* et al. in 2008 [zha08a,zha08b].

Atmospheric pressure plasma cleaning of glasses

Atmospheric pressure plasma has a high potential for cleaning glass surfaces by the removal of organic contaminations, which are adsorbed due to common environmental conditions [lan18]. Here, the main contaminations are hydrocarbons (C_xH_y, where $x < y$). A number of different mechanisms can be utilised for plasma-induced cleaning since generally plasma provides radicals, ozone (O_3), negative and positive ions, free electrons and a certain amount of ultraviolet irradiation and thermal impact. As an example, hydrocarbons can be removed chemically when applying O_2 as plasma process gas. By the plasma discharge, O_2 is dissociated to excited, radical oxygen atoms (O^*) and subsequently reacting with surface-adherent hydrocarbons according to

$$(-CH_2 - CH_2 -) + 6O^* \rightarrow 2CO_2 + 2H_2O. \qquad (2.2)$$

Beyond chemical cleaning, physical cleaning can be achieved using inert process gases due to ion bombardment and electron sputtering. Such cleaning is of specific interest for medical and biological applications as for example for preparing object holders for microscopic analysis or for plasma-sterilisation of injection needles or surgery devices [che10].

The removal of carbonic contaminations from glass surfaces by atmospheric pressure plasma cleaning was presented by *Shun'ko* and *Belkin* in 2007. According to the experimental setup as described by the authors, the plasma source was a capacitively coupled DBD plasma jet, driven at 13.56 MHz radio frequency and a power of 300 W. As process gas, O_2 (2%) was admixed to the carrier gas, Ar (98%), where the gas flow velocity was approximately 6 m/s. By such treatment of glass substrates, which were placed about 10 mm below the plasma source nozzle outlet, efficient cleaning as confirmed by a rapid increase in the sample wettability by a factor of approximately 8 was achieved after a plasma treatment duration t_{plasma} of merely one second [shu07].

Comparable results were reported by *Iwasaki* et al. in 2008 applying a multiple nozzle jet atmospheric pressure plasma source based on a glow discharge. This plasma source was operated at a voltage of 10 kV and a frequency of 60 Hz. Using a gas mixture of Ar (99%) and O_2 (1%) at a flow rate of 15 slm, the contact angle on glass substrates was reduced from approximately 50° to approximately 8° after a plasma treatment duration of 23 ms [iwa08a]. This reduction in contact angle was stated to be due to the removal of organic contaminants from the sample surfaces. In further work, the authors confirmed this assumption by X-ray photoelectron spectroscopic (XPS) analysis of plasma cleaned glasses. For this purpose, plasma treatment was performed using a planar DBD jet, driven at a frequency of 40 kHz and a power of 300 W. As process gas, a mixture of N_2 and O_2 was applied, where the particular flow rates were 40 slm (N_2) and 0-0.08 slm (O_2), respectively. The working distance from the plasma source outlet to the glass sample surface was 5 mm. The presented change in chemical composition of the sample surface as determined by XPS showed a high correlation with the measured contact angles, where a decrease in the percentage of carbon implicated a decrease in contact angle. Based on these findings, the authors showed that oxygen-based species such as ozone or radicals have a remarkably higher impact on the glass cleaning efficiency than nitrogen species [iwa08b]. The maximum cleaning efficiency was found for an O_2 admixture of 0.03% to the carrier gas, N_2. Here, carbon was reduced by a factor of approximately 1.6; the contact angle was 8-times lower with respect to untreated glass.

In 2008, *Buček* et al. reported on atmospheric pressure plasma cleaning of glass using a diffuse coplanar surface barrier discharge (DCSBD) source. Here, a thin plasma sheet with a thickness of approximately 500 µm was ignited on the dielectric surface. Since the distance of the glass sample to the dielectric was 300 µm, the plasma was in direct contact with the investigated glass surface. Experiments were performed in a discharge power range from 300 to 525 W, applying ambient air, pure N_2 and pure O_2 as process gases. For all three gases, the contact angle was reduced by a factor of approximately 3.5 after a plasma treatment duration of five seconds. Successful cleaning was further confirmed by secondary ion mass spectroscopy (SIMS) and XPS, where a considerable decrease (max. 13-times) in characteristic peak intensities of relevant organic fragments was observed [buc08].

To summarise it can be stated that atmospheric pressure plasma methods are suitable for removing organic contaminations from glass surfaces. Depending on the applied plasma parameters, either hydrophilic or hydrophobic surfaces can be realised since plasma cleaning usually involves a change in contact angle and surface energy, respectively, as presented in more detail in the following sub-section. Plasma surface cleaning and an accompanying hydrophilisation have thus gained importance in the production of flat display-panels or coating processes of facade windowpanes. Atmospheric pressure plasma can moreover be applied in order to remove lacquer coats such as graffiti and acrylic resin from glass surfaces as for example in restoration [mai07] or urban renewal.

Atmospheric pressure plasma activation of glasses

In contrast to plasma-induced cleaning, the aim of plasma activation is a chemical modification of the treated surface. Besides chemical reduction and oxidation, attaching functional groups and/or molecular chains onto the surface by plasma polymerisation is a common application. As an example, oxygen plasmas are used for generating surface-adherent polymerised hydroxyl groups (-OH) or carboxyl groups (-COOH) in order to graft pharmaceuticals as reported by *Cheruthazhekatt* et al. in 2010 [che10]. Another widespread application of plasma activation is the modification in wettability [cer09]. As already discussed above, the contact angle of both a sample surface and test liquids is one of the most commonly-used indication value for successful cleaning. Since the contact angle is directly related to the surface energy and its polar and disperse fractions, respectively, it is also suitable for describing activation effects such as a change in surface polarity [hom13].

In 2004, *Yamamoto* et al. reported on atmospheric pressure plasma-induced hydrophilisation and hydrophobisation of sodium silicate glass where the intended application was to substitute windscreen wipers. As plasma source, a DBD reactor was used, driven at a voltage of 20 kV and a frequency of 60 Hz. Three process gasses, dry air, pure N_2, and He, were applied at different flow rates. The distance from the high-voltage electrode to the glass sample surface was kept constant at 3 mm. It was shown that using this setup, the contact angle was decreased from 45° to 10° after a plasma treatment duration of 10 seconds, reaching its saturation value of 4° after 60 seconds. Further, dry air was identified to represent the most appropriate process gas whereas the flow rate did not influence the resulting contact angle. However, the obtained decrease in contact angle showed a poor durability. After mechanical attrition tests for 5 days, the hydrophilic effect was completely lost. The same behaviour was observed for hydrophobised samples [yam04].

A long-term stable increase in hydrophobicity of glass surfaces using a coplanar DBD setup was presented by *Fang* et al. in 2006. Here, the dielectric separation of both electrodes was realised by the glass sample itself where the discharge gap was 1.5 mm. In addition to the process gas, ambient air, a polydimethyl siloxane fluid was applied to the glass surfaces. In this way, a hydrophobic layer was generated by plasma activation and the interaction of the involved molecules of both the glass surface and the adherent fluid. Experiments were performed at a voltage of 10 kV, resulting in an increase in contact angle from 53° to maximum 122° after a treatment duration of 11 minutes. By applying *Fourier* transform infrared (FTIR) spectroscopy it was ascertained that a new material, consisting of $-CH_3$-containing groups, was chemically bonded to the glass surface, resulting in long-term stable hydrophobic properties [fan06b].

2.2 Interactions of laser irradiation with glasses

Generally, material evaporation due to pulsed laser irradiation at adequate fluence is referred to as laser ablation. Due to the rapid laser-induced heating of the material surface, a plasma plume is formed during laser ablation, whereas no plasma occurs during laser desorption. The ablation behaviour of any medium and glasses in particular is strongly dependent on both the wavelength λ and the pulse duration τ of the incoming laser irradiation.

Glasses typically feature a high transmission T in the visible (VIS) and near infrared (NIR) wavelength range ($T > 80\%$ from approx. 170 to approx. 2000 nm in the case of fused silica). An appropriate approach for pure laser ablation at low fluence is thus to employ far ultraviolet (FUV) or mid infrared (MIR) laser irradiation. Against this background, fluorine (F_2) excimer lasers (FUV, $\lambda = 157$ nm) are suitable for micro structuring of fused silica as reported by *Ihlemann* et al. in 2003 and 2007 [ihl03, ihl07]. Here the ablation threshold amounts to approximately 1 J/cm². Material removal of fused silica using carbon dioxide (CO_2) lasers (MIR, $\lambda = 10.6$ µm) is a photo-thermal ablation process, based on fracturing of the glass surface by laser-induced thermal stress, melting and evaporation [bue90]. However, the formation of stress-produced micro cracks can be avoided by heating the glass work piece to be machined as presented by *Yen* et al. in 2006 [yen06]. In addition to material removal for micro structuring, controlled localised CO_2 laser-induced melting and material flow can be used for smoothing and repairing damages on glass surfaces as shown by *Mendez* et al. in 2006 [men06]. Regarding the ablation of fused silica, the authors reported an ablation threshold intensity of 100 kW/cm² at a pulse duration of 300 µs.

Besides the choice of highly-absorbed laser wavelengths, the use of laser pulses of ultra-short duration is an appropriate way for improving laser ablation of dielectric, transparent media. Here, nanosecond pulses provoke heating of a thin near-surface layer within the pulse duration, resulting in sudden evaporation and the formation of an ionised ablation plasma plume. As a consequence of such heating, disturbing effects such as the formation of re-deposited debris, micro cracks (see above) and burrs can develop. Further, the incoming laser irradiation is usually attenuated by the laser-induced plasma plume due to absorption and scattering at debris particles as well as plasma shielding in the case of high electron densities, consequently resulting in a decrease in ablation rate. The disturbing effects arising during nanosecond ablation can be overcome by applying laser pulses in the picosecond [ger08] and femtosecond [ute11] range. Here, material removal occurs much faster than heating of deeper regions within the bulk material due to the short pulse duration. Relating to ultra short pulse laser ablation, the interaction of both the solid and the incoming laser irradiation can be described by a two-temperature model: First, the energy of the photons is absorbed by electrons. Second, the absorbed energy is transferred to the network, initiating material removal [lad02]. Such material removal is due to ionisation processes within the network and subsequent *Coulomb* explosion[2]. As a result, the network temperature remains constant during absorption of the incoming ultra short laser pulse [gib96]. The improved coupling of energy during ultra short pulse ablation is visualised by the pulse duration-dependent damage threshold fluence of fused silica as reported by *Perry* et al. in 1999 [per99] in figure 2.2.

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[2] *Coulomb* explosion describes the desorption of electron-depleted atoms due to repulsion forces.

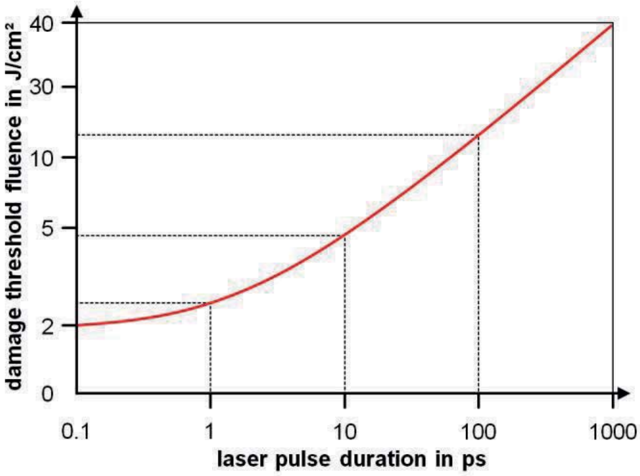

Fig. 2.2: Damage threshold fluence vs. laser pulse duration at a wavelength of 1053 nm, data taken from [per99]

However, in comparison to picosecond and femtosecond laser sources, nanosecond lasers stand out due to a high efficiency as well as low acquisition and maintenance costs. Owing to these advantages, several hybrid ablation methods based on such laser sources were developed in the last decades in order to improve nanosecond laser ablation of transparent media as presented hereafter.

Laser-induced plasma-assisted ablation (LIPAA)

Laser-induced plasma-assisted ablation (LIPAA) is achieved by several plasma interactions at the rear side of the glass sample to be ablated. For this purpose, a laser beam is focussed onto a metallic target surface in order to ignite a plasma-induced ablation plume. As shown in figure 2.3, the glass sample is placed below the metallic target.

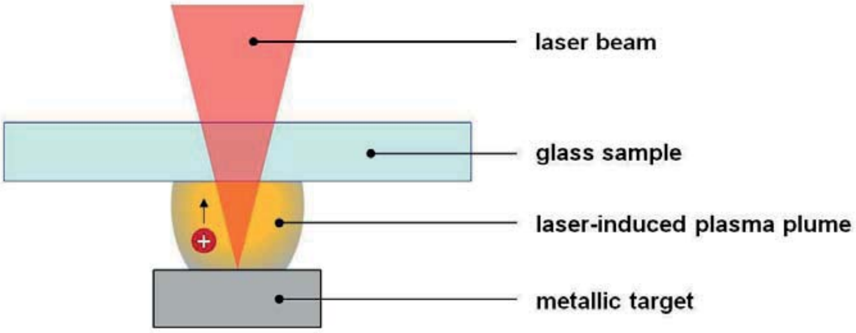

Fig. 2.3: Functional principle of laser-induced plasma-assisted ablation (LIPPA)

LIPPA was first reported by *Zhang* et al. in 1998. Here, a 4th-harmonic Nd:YAG laser at a wavelength of 266 nm and a pulse duration of 6 ns was applied. Experiments were performed in a vacuum chamber (10^{-1}-10^{-2} Pa) on 0.6 mm-thick fused silica samples; the metallic target was made of stainless steel. The authors observed a strong dependency of the ablation threshold fluence and the etch rate on the distance between both the metallic target and the sample's rear side. At the lowest investigated distance of 20 µm, the ablation threshold fluence was 0.5 J/cm² whereas the etch rate was determined to amount to approximately 35 nm/pulse. In further work it was moreover shown that