Original Paper

Machining of silica glasses using excimer laser radiation[1)]

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Various silica glasses were engraved deliberately by excimer laser radiation using wavelengths of 308 and 248 nm. The ablation of different samples was investigated by systematic variation of the processing parameters. The ablation rates were determined using profilometry and gravimetric measurements by evaluating the processing quality and the morphology of the processed surfaces was considered. The phenomenon of ablation is explained as a non-linear interaction of the laser beam and the glass. The experimental results show that the ablation behaviour of silica glass depends on the wavelength and the intensity of the laser radiation, on the surface quality and the degree of purity of the glass. Although high ablation rates were obtained, the suitability of excimer lasers for micromachining is restricted due to the rough surface morphology and poorly defined edges.

Excimerlaserstrahlbearbeitung von Kieselglas

Unterschiedliche Kieselgläser wurden mit Excimerlasern der Wellenlängen 308 und 248 nm bearbeitet. Eine systematische Variation der Bearbeitungsparameter ermöglichte die Untersuchung der Abtragsphänomene. Die Abtragsraten wurden mit einem Oberflächenmeßgerät und gravimetrisch ermittelt. Anhand der Oberflächenmorphologie und der Kantenschärfe wurde die Bearbeitungsqualität beurteilt. Als Ursache für den Materialabtrag wird eine nichtlineare Wechselwirkung zwischen der Laserstrahlung und dem Kieselglas diskutiert. Die experimentellen Untersuchungen ergeben, daß das Abtragsverhalten von der Wellenlänge und der Intensität der Laserstrahlung, aber auch von der Oberflächenqualität und der Zusammensetzung des Glases abhängt. Obwohl große Abtragsraten auftreten, können Excimerlaser aufgrund der zerklüfteten Oberflächen und der schlechten Kantenqualität nur in eingeschränktem Umfang zur Mikrobearbeitung von Kieselgläsern eingesetzt werden.

1. Introduction

Silica glasses exhibit optical, mechanical and thermal properties which meet high material demands. They show good optical translucency from the ultraviolet to the infrared range of the spectrum, very low thermal expansion and heat conductivity, high elasticity, low dielectric losses, high thermal shock resistance and high transformation and softening temperature ranges. However, processing silica glasses is difficult: their high viscosity and high processing temperatures are undesirable for conventional melting and forming. Silica glasses are chemically resistant and etching is only possible by the use of fluoric acid.

Mechanical processing of the hard glass is carried out with diamond tools which can introduce undesirable impurities into the glass as a result of the hard tool materials and the cooling oil.

Laser processing of materials is an alternative to conventional methods and does not apply a force to the material, the processing tool being the energy of the laser beam. An example of an industrial application is using the CO_2 laser beam to cut silica glasses during the production of car lamps [1]. Compared to CO_2 and solid state lasers, excimer lasers can produce shorter wavelengths, high pulse powers and short pulse durations. Typically a thin layer of material of less than one micron thickness is removed by each pulse from the excimer laser which reduces the heat-affected zone in the material and allows greater accuracy of sample treatment. Therefore, excimer lasers are used for micromachining and applications are found in the microelectronics industry, e.g. for the exposure of photolac and the structuring of thin insulating films in integrated circuits [2 and 3]. Structures of 0.3 μm have been obtained using excimer laser radiation in microlithography [2]. A systematic investigation into the interaction of XeCl excimer laser radiation with glass [4] demonstrated that certain glasses can be micromachined very precisely. It has been shown that an additional reactive gas increases the ablation rates of silicate glasses by 50 % compared to the ablation in air [5].

The aim of this work was to study the influence of the laser and the material parameters on the micromachining of silica glass.

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2. Interaction between UV laser radiation and silica glass

Silica glass, an insulator, has only bound electrons and is UV-translucent, except in the resonance case. The most important resonance arises from the transition of electrons from the valence band to the conduction band. The band gap of silica glass is 9 eV [6], which is therefore above the photon energies of the excimer laser radiation 4 eV (λ = 308 nm), 5 eV (λ = 248 nm) and 6.4 eV (λ = 193 nm), respectively, and these photon energies are not large enough to result in electronic transitions. The absorption of the excimer laser radiation at low energy densities in silica glass is correspondingly small (absorption coefficient $\beta_{308\ \text{nm}} \approx 0.25\ \text{cm}^{-1}$).

For higher intensities of laser radiation the optical properties of the glass become irradiance-dependent due to non-linear effects. As a consequence the absorption coefficient increases dramatically, possibly causing material damage by explosive ablation. This effect is induced by the production of free electrons due to non-linear processes, namely by multiphoton interband transitions or by impact ionizations. Multiphoton ionization is more probable at shorter wavelengths and with high photon densities. The presence of some primary free electrons is required in order to start an avalanche of free carriers for impact ionization and these electrons can be produced via multiphoton processes. For either impact ionization or multiphoton ionization a minimum intensity of the laser radiation must be exceeded [7]. This intensity, expressed in term of energy density, is called the ablation threshold of the material.

When an avalanche of free carriers has developed, a microplasma is formed and explosive damage of the material occurs in most of the cases which is known as an optical breakdown. When the optical breakdown occurs in the cold gas environment above the target, it is termed a laser-induced gas breakdown [7].

During ablation a large plasma evolves from the ionized material and it expands vertically away from the target surface towards the laser beam. The plasma cloud interacts with the laser beam itself, if the density of electrons and particles in the plasma is high enough. Part of the laser radiation is absorbed or scattered, but the remaining part reaches the target.

A less dramatic process of non-linear absorption, which takes place below the ablation threshold, is the formation of colour centres in silica glasses [8 to 11]. Colour centres arise from oxygen vacancies, the energy being delivered by two-photon processes. This effect is reported only for the ArF (λ = 193 nm) and the KrF (λ = 248 nm) excimer laser radiation, not for the XeCl (λ = 308 nm) excimer laser radiation.

The absorption process in commercial silica glass can be characterized as a "surface effect": The excimer laser beam always couples into the surface. The reduced bonding energies at the phase boundary of the surface enable non-linear absorption processes at lower intensities. The probability of multiphoton ionization is enhanced on rough surfaces due to the increased density of defect states [12]. Cracks in dielectrics result in a local increase of the electrical field amplitude and therefore reduce the threshold intensity for impact ionization and for optical breakdown [7]. The experimental work aims therefore at the investigation of the influence of the surface quality of silica glass on the ablation phenomena.

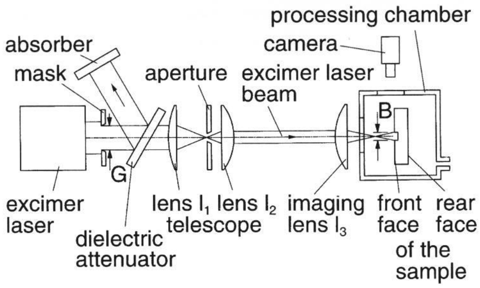


Figure 1. Schematic of mask projection. G: mask size, B: image dimension.

3. Experimental

Pulsed high-power XeCl (λ = 308 nm) and KrF (λ = 248 nm) excimer lasers were used for the present investigation. The XeCl excimer laser is characterized by a pulse duration of 50 ns, a maximum pulse energy of 2 J and a uniform intensity distribution with a rectangular cross-section. A shorter pulse duration of 29 ns and a maximum pulse energy of 0.5 J are characteristic for the KrF excimer laser. For processing samples a mask was projected on the target, producing an area which was irradiated with a high energy density (figure 1). The image size, i.e. the size of the irradiated area, was adjusted by the imaging ratio B/G, where B is the image size and G the mask size. A dielectric attenuator reduced the energy density H_E at the workpiece.

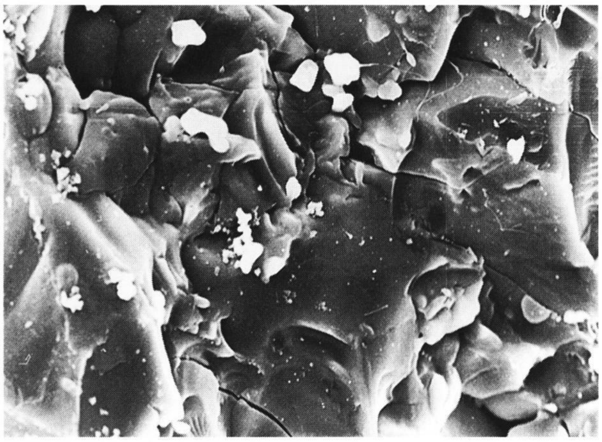
Experiments in a low-pressure atmosphere were performed using a processing chamber, which was evacuated down to a pressure of 1 Pa. The sample holder was heated in order to remove adsorbed layers from the surface of the glass, whilst a camera monitored the plasma above the workpiece.

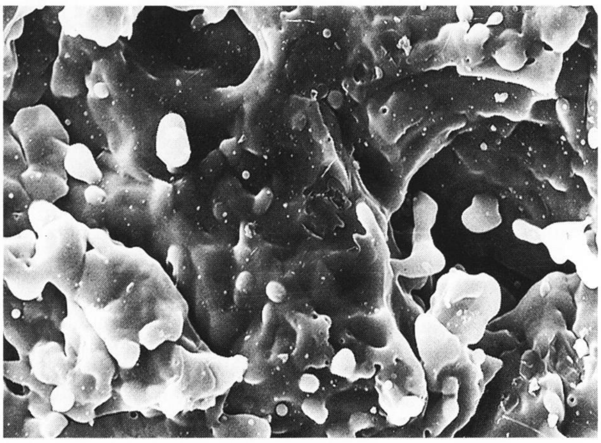
The compositions of the investigated silica glasses (Suprasil, BQ-B and HOQ) differed due to the different manufacturing processes and raw materials (table 1). The optical behaviour of silica glass is influenced by Si−O atomic resonance oscillation (IR absorption bands), a transition due to the bridging oxygen electron (UV edge), impurities and defects in the network structure. The OH concentration of the samples was determined by IR spectroscopy using the band at 2.75 µm [13]. Suprasil exhibited the highest OH concentration, whereas it was lower for BQ-B glass and negligible for HOQ glass.

Both BQ-B glass and HOQ glass are melted from natural crystalline raw materials. An absorption band at 237 nm (5.2 eV) was measured for these glasses. The origin and the exact position of this band are still not clarified but it is thought to result from the presence of metallic impurities [13] and oxygen vacancies [7 and 10]. The synthetically produced Suprasil did not show this absorption band.

Table 1. Degree of impurities of the silica glasses

	Suprasil	BQ-B	HOQ
OH concentration	1200 ppm	200 ppm	<30 ppm
metallic impurities		550 ppm	50 ppm
other impurities	Cl	alkali	bubbles, inclusions
production process	flame hydrolysis	H_2/O_2 flame	electric furnace
raw materials	$SiCl_4$	——— natural crystalline raw materials ———	





Figures 2a and b. SEM micrographs showing a typical surface morphology of HOQ glass obtained using an XeCl excimer laser (λ = 308 nm) with a) low energy density (H_E = 7.4 J/cm^2, 10 pulses); b) high energy density (H_E = 28.5 J/cm^2, 10 pulses).

Samples with rough surfaces (mean roughness R_Z = 2.5 μm) and with polished surfaces (R_Z = 0.25 μm) were prepared in order to study the influence of the surface quality on the processing results.

The ablation depth was normally measured using a mechanical surface profilometer. For comparison gravimetric measurements of the samples before and after processing were also performed. The ablation depth was calculated from the density of the glass and from the image size. Ablation rates were obtained from the ablation depths and the pulse numbers.

4. Results and discussion

4.1 Ablation behaviour

Above the ablation threshold ($H_E \approx$ 2 to 4 J/cm^2) a higher surface roughness of the silica glass in the ablated area was obtained. The morphology of HOQ glass was characterized by shell-shaped breaks and cracks that also decreased the edge quality for micromachining (figure 2a). Irradiation with higher energy densities far above the ablation threshold caused a smoother topography and very small droplets on the surface (figure 2b). This melting effect could be explained by a larger amount of energy being deposited by the laser beam in the glass. Additionally, the thermal radiation from the plasma cloud was more significant at higher intensities of the laser beam. Similar effects occurred for the XeCl excimer laser processing of Suprasil and BQ-B glass.

In figure 3 the ablation rate of HOQ glass and the standard deviation from three measurements are plotted as a function of the energy density. Three regions could be distinguished: In the "optical translucent region" at low energy densities ($H_E \leq$ 2 J/cm^2) uniform ablation or at least local surface damage was not observed. In the "threshold region" damage occurred on the surface. Due to the non-uniform processing the ablation rates could not be determined. In the "plasma region" above the ablation threshold material was uniformly ablated and a plasma was formed at the surface.

In general the ablation rates of silicate glasses [4] are very high compared to the ablation rates of metals [14] and ceramics [15]. The reason for the high ablation rates obtained was probably an optical breakdown in the glass that occurred during irradiation. This explanation is supported by the morphology of the processed surface that appeared to be caused by explosive damage.

After a maximum value near the ablation threshold the ablation rates decreased with increasing energy density. This unusual behaviour has also been observed for the excimer laser processing of borosilicate glass [16] and other glasses with low absorption coefficients [4]. The interaction between the excimer laser beam and the plasma may have contributed to this phenomenon. At energy densities near the ablation threshold the plasma was translucent and most of the energy of the laser beam reached the surface of the glass. High energy densities resulted in an optically dense plasma shielding the glass from the laser beam and causing lower ablation rates.

4.2 Influence of the intrinsic sample composition

The ablation rate of Suprasil was more than 1 µm/pulse lower than the ablation rate of HOQ glass (figure 4) and the ablation threshold was higher ($H_E \approx 2$ to $6\,J/cm^2$). Suprasil contains only a small amount of metallic impurities, inclusions and bubbles. The higher OH content of Suprasil seemed to compensate for these intrinsic defects and increased the resistance of the glass to radiation. Similar observations have been made by other authors [8 and 17]. It is therefore the "surface effect" that coupled the XeCl excimer laser radiation into the glass.

BQ-B glass contains a lot of metallic impurities and bubbles and it exhibits a medium OH concentration. Again the ablation threshold was shifted to higher energy densities (compared with HOQ glass) and the ablation rate was lower.

4.3 Influence of the surface quality

The ablation threshold of the polished glass was generally shifted to higher values compared with the threshold of rough glass surfaces. Rough surfaces make the coupling of the excimer laser beam easier. They offer a geometric multiplying of the "surface effect" by multiple reflections of the laser beam. Irregular crater formation was often observed within the irradiated area of polished samples when energy densities in the threshold region were used instead of a homogeneous ablation with the shape of the projected mask. This behaviour can be described as a "germination effect": On the polished surface small holes evolve from the remaining polishing scratches (figure 5).

Silica glass samples are also ablated at the rear face, if the thickness is not too large [4]. An amplification of the intensity of the laser beam on the rear face due to interference effects has been proposed as an explanation for this effect [18]. Additionally, the authors' experiments have demonstrated that the surface quality also influences the ablation rate of the rear face with unpolished rear faces resulting in higher ablation rates than polished rear faces.

4.4 Influence of the excimer laser wavelength

A better processing quality was obtained using 248 nm excimer laser radiation when the surface showed smaller shell-shaped breaks (figure 6) compared with the machining using 308 nm excimer laser radiation (figure 2a). The improved morphology could be explained by lower ablation rates for the 248 nm excimer laser radiation (figure 7).

The decrease of the ablation rates with decreasing wavelength, which has been observed for the excimer laser machining of metals, has been explained by smaller absorption lengths at shorter wavelengths [14]. This cannot explain the decrease of the ablation rates for the excimer laser processing of silica glass, because non-linear

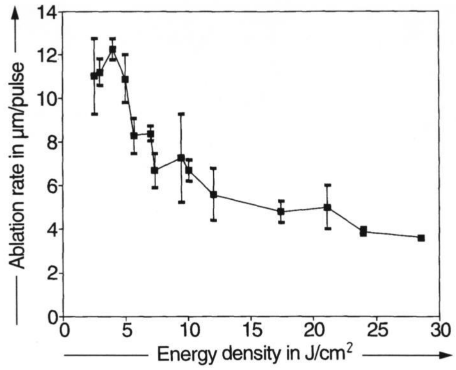


Figure 3. Ablation rate of HOQ glass as a function of energy density, XeCl excimer laser ($\lambda = 308$ nm).

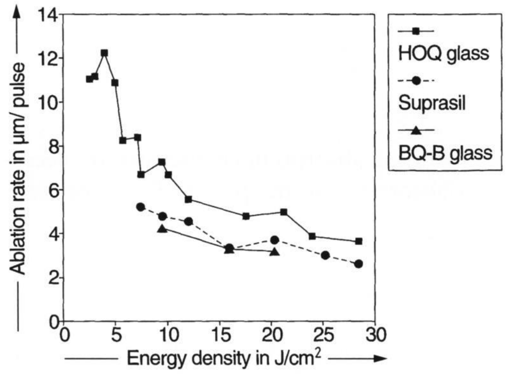


Figure 4. Ablation rate of different silica glasses as a function of energy density, XeCl excimer laser ($\lambda = 308$ nm).

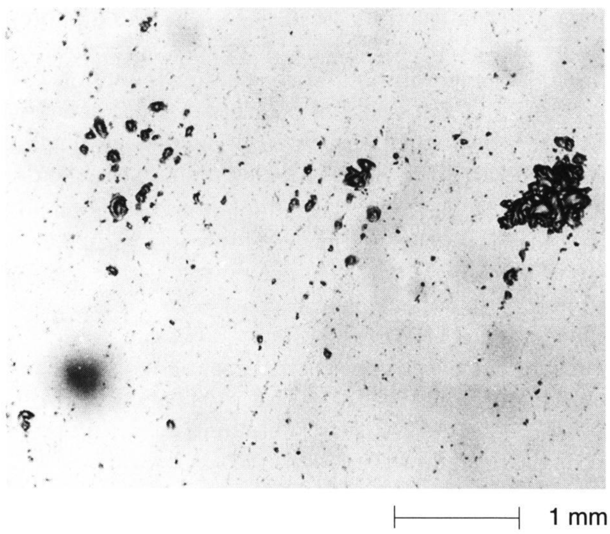


Figure 5. Optical micrograph showing the "germination effect" on the surface of BQ-B glass due to existing surface damage, XeCl excimer laser ($\lambda = 308$ nm), $H_E = 6.1\,J/cm^2$, 500 pulses.

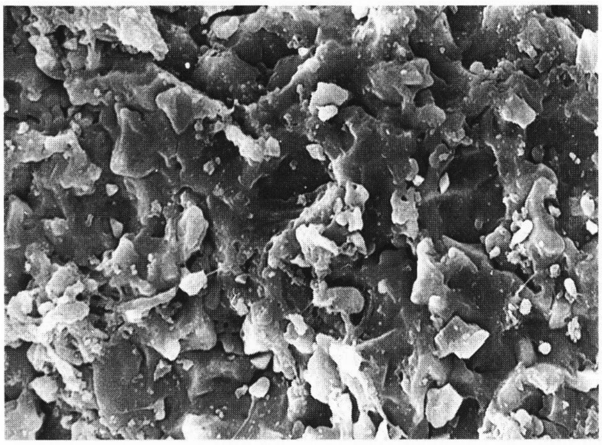


Figure 6. SEM micrograph showing a typical surface morphology of HOQ glass obtained using low energy density, KrF excimer laser (λ = 248 nm), H_E = 7.4 J/cm^2, 10 pulses.

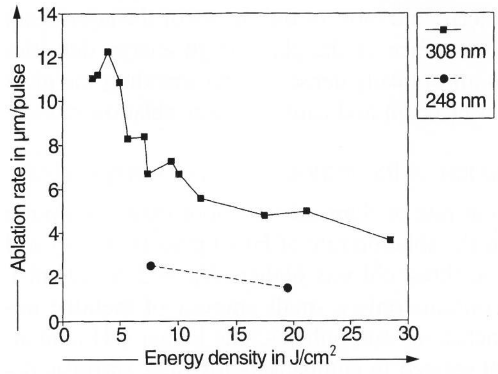
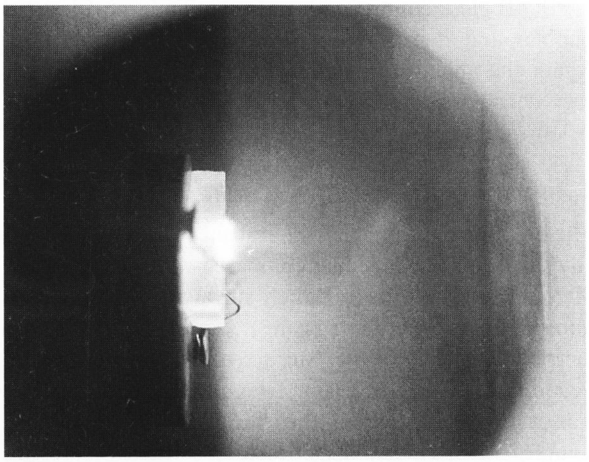


Figure 7. Ablation rates of HOQ glass as a function of energy density at different wavelengths.

and strongly modified absorption coefficients are necessary to obtain absorption in the practically transparent glass.

A different ablation mechanism is proposed as follows [9]: Multiphoton processes are necessary for the production of free electrons, at least of the primaries. The time Δt for the incidence of two or three photons is lower for higher frequencies ($\Delta t = 2\pi/\omega = \lambda/c$). As a consequence the probability for absorption processes is higher for the 248 nm excimer laser radiation than for the 308 nm excimer laser radiation. Therefore, a lower photon density is necessary to damage the glass [9]. Assuming a band gap of 9 eV in silica glass and a photon energy of 5 eV (λ = 248 nm), two-photon processes are necessary for absorption. For a photon energy of 4 eV (λ = 308 nm) three-photon processes are necessary for absorption, but they are less likely and require higher photon densities resulting in higher damage thresholds.

Further evidence for the multiphoton absorption and an electron avalanche at shorter wavelengths has been given by Ihlemann [18]. He demonstrated that the ablation rates for the 248 nm excimer laser radiation ablation of silica glasses with 500 fs pulses are one order of magnitude lower than for the ablation with pulses of some nanoseconds duration. An explanation could be given as follows: For pulse durations in the range of 500 fs the breakdown cannot take place, because the avalanche build-up time is in the range of 0.1 to 1 ns. In this case multiphoton absorption dominates which is an "instantaneous" process and results in lower ablation rates.



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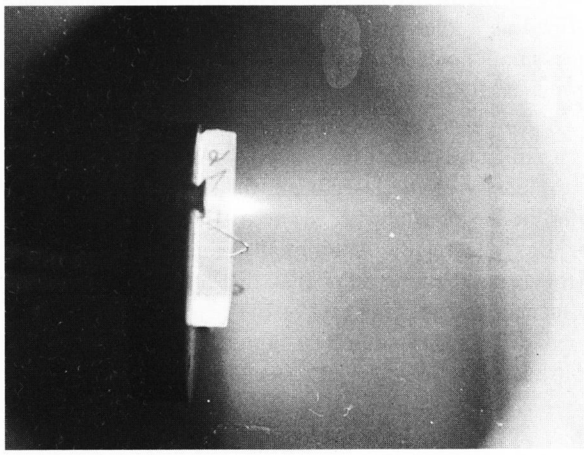

b)

Figures 8a and b. Plasma above the HOQ glass surface a) in normal atmosphere, b) in vacuum.

4.5 Influence of the atmosphere

The shape of the plasma was strongly influenced by the atmosphere in the processing chamber. In air the plasma remained close to the surface (figure 8a). In vacuum the plasma expanded further from the sample due to a reduced probability of collisions with gas molecules (figure 8b). The ablation thresholds, the ablation rates and the surface morphology were not influenced by the ambient atmosphere (air and vacuum, respectively).

5. Conclusion

The processing of silica glasses is influenced by the energy density and the wavelengths of the excimer laser radiation. At low energy densities the silica glasses investigated transmit the laser radiation and intrinsic damage inside the glass does not occur.

Non-linear processes are responsible for the absorption of the laser radiation, when a certain energy density is exceeded. The surface of the sample is destroyed by ablation of the material. The ablation threshold depends on the excimer laser wavelength, the material and the surface quality. Rough surfaces exhibit lower ablation thresholds compared with smooth glass surfaces which can be explained by multiplication of the surface effect.

Maximum ablation rates are obtained using energy densities slightly above the ablation threshold and typically layers of 3 to 12 μm thickness are ablated per pulse. The ablation rate is influenced significantly by the surface quality and the number of intrinsic defects and impurities in the glass. Rough surfaces with cracks are obtained using 308 nm excimer laser radiation. The 248 nm excimer laser processing offers smoother surface morphologies and also lower ablation rates.

6. References

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