

Challenging Glass 7 Conference on Architectural and Structural Applications of Glass Belis, Bos & Louter (Eds.), Ghent University, September 2020. Copyright © with the authors. All rights reserved. ISBN 978-94-6366-296-3, https://doi.org/10.7480/cgc.7.4485



# Experimental Investigation into SLS Glass Surface Modification Using KrF Excimer Laser

Shahryar Nategh<sup>a, b</sup>, Pieter Vijverman<sup>a</sup>, Jeroen Missinne<sup>b</sup>, Jan Belis<sup>a</sup> <sup>a</sup> Department of Structural Engineering and Building Materials, Ghent University, Belgium, Shahryar.nategh@ugent.be

<sup>b</sup> CMST, Ghent University and imec, Belgium

Glass is a brittle material and any damage or modification of its surface may have a profound impact on the strength. To modify the glass surface, the precision of the instrument is determining for achieving the most reliable results. Nowadays, laser technology as a non-contact tool is employed as a glass cutting, drilling and holing tool in many applications such as sensors and optical communications. Along with high speed, flexibility, and scalability, lasers with short pulse duration can break the interatomic bonds before perturbing the lattice. Among lasers, excimer micromachining lasers have some advantages in terms of surface morphology, including depth control, edge quality, and minimizing peripheral thermal damage as the ablation process is more likely to be material-removing instead of heating. This article aims to examine the interaction of krypton fluoride (KrF) excimer laser with the soda-lime silica (SLS) glass by fabricating grooves and microholes.

Keywords: Soda-lime silica (SLS) glass, Laser ablation, KrF excimer laser

#### 1. Introduction

Changing the surface of glass plays a key role in its mechanical strength. This change can happen locally or in a large area during life service, also in different geometries. There are different ways to produce artificial damage and investigate its effects on glass structures. Among contact-induced damage, indentation (Schneider et al. 2017) and sand abrasion (Datsiou and Overend 2017a, 2017b) are used to resemble, e.g., the scratch creation and exposure to weathering action, respectively. On the other hand, lasers as a non-contact technique are also employed to modify transparent materials such as various types of glasses, mostly because of their precision, scalability (machining large surfaces), reproducibility (e.g. generating similar lines with same specifications) and high speed (Gattass and Mazur 2008). In this sense, lasers can be used for bulk glass modification (Righini and Chiappini 2014), laser-assisted chemical etching (Gottmann et al. 2017), and material removal from the surface by means of ablation (Ben-Yakar and Byer 2004). Therefore, if we are able to generate artificial damage with specific dimensions and minimal detrimental side effects (e.g. cracks), characteristic investigations will be attainable.

Laser ablation results from laser-induced optical breakdown, a process by which the laser beam energy is transferred to the substrate to remove the material from the surface by either heating and evaporating the material or breaking the electron bonds, depending on the type of laser (Van Steenberge et al. 2005). Laser pulse duration is the main parameter that influences the form of interaction between laser beam and material. This duration can vary over the range of nanoseconds to femtoseconds. As a result, pulsed lasers can be categorized as short-pulsed (nanoseconds) and ultrashort-pulsed (pico- and femtoseconds) lasers. When a laser pulse meets the material, electrons absorb its energy and once the absorbed energy exceeds the sublimation energy, the material particles evaporate and become vaporized particles (single-photon absorption) (Nieto et al. 2015). For ultrashort pulsed lasers, the electrons do not have time to diffuse the energy to the lattice as the next pulse comes quickly and adds energy to the previous one which increases the energy level until the atomic bonds are broken (multi-photon absorption) (Ahsan et al. 2013). Although ultra-short pulsed lasers have advantages with respect to precision, the control over the cross-sectional geometry of lines is limited to some extent.

A KrF Excimer laser employs a gas as gain medium to achieve the ultraviolet (UV) or deep UV region of the spectrum with nanosecond pulse durations and is capable of achieving high pulse energies. Laser wavelength in the (deep) UV where most materials heavily absorb the light allows machining wide ranges of materials, i.e., high absorption and low penetration depth of the laser light. Therefore, it is possible to fabricate fine patterns with very high resolution in depth with the help of masks (Rudolph et al. 2007) provided that the laser beam is homogenized by a special optical system before being used for machining. At present, excimer lasers fabricate the finest microfeatures possible with the aid of masks. The excimer gain medium is a mixture of a rare gas (e.g. argon, krypton, or xenon), a halogen (e.g. fluorine or chlorine), and a buffer gas (helium and/or neon) (Basting and Marowsky 2005). The krypton fluoride (KrF) and argon fluoride (ArF) excimer lasers are among the most important lasing species which have been used frequently

# **CG** Challenging Glass 7

in polymer (Dyer 2003) and glass micromachining (Karstens et al. 2016; Liu et al. 2012). So far, the substrate of most excimer laser ablations were thermal resistant glasses such as fused silica and borosilicate (Chen et al. 2005; Tseng et al. 2007) because of their low coefficient of thermal expansion and resistance to thermal shocks. However, in structural applications, soda-lime silica glass is the most prevalent type of glass which accounts more than 95% of manufactured glass in Europe (Glass Alliance Europe 2018) because of its low cost, capability of being re-softened a number of times, and reasonable hardness. However, precise, high-resolution laser patterning of soda-lime silica glass is still a challenging task (Zhang et al. 2009).

To ablate a high precision and high-quality structure at micrometer scales, the interaction between the laser and the glass must be well understood and controlled. The aim of this paper is to modify the surface of soda-lime glass using KrF excimer (248 nm) laser to shed light on the behaviour of soda-lime glass under laser ablation in terms of crack appearance and depth control. Different laser parameters have been studied and the results are examined using microscopes and profilometers.

## 2. Experimental method

Commercially available 4 mm-thick soda-lime silica glasses were used. Samples with the dimensions  $10 \times 10$  cm were cleaned with isopropyl alcohol (IPA) wiping before experiments. The tin side of glass recognized by UV light inspection is chosen for all laser ablations in this paper. The irradiation source is the KrF excimer laser (ATL Lasertechnik SP300i) with 248 nm emission wavelength. The schematic drawing of the laser delivery path is depicted in Fig. 1. The specifications of this laser system are listed in Table 1. The approximately  $6 \times 4$  mm rectangular laser beam can be modified to any shape according to the mask of the projection system. A square mask aperture  $3 \times 3$  mm and projection lens with the demagnification of 10 are used to obtain a homogeneously irradiated spot of  $300 \times 300$  µm on the sample. The speed of ablation is set to generate 30 pulses per area to shape a line ablation and 1 pulse per area for separate spots. A pulse repetition rate of 100 Hz was fixed during ablation. The fluence is varied using a dielectric attenuator and checked with a sensor before each test. The samples were again cleaned after ablation with IPA to reduce the debris pile-up on the surface.

The depth of the ablation is measured with either a non-contact optical profiler (WYKO NT3300) or a mechanical stylus profilometer (Tencor Alphastep 200) based on the depth and roughness of ablation. WYKO, as a white light interferometer, is capable of mapping several square millimeters wide area in a single measurement, with sub-nanometer resolution, providing instantaneous information about surface roughness, shape, and waviness.



Fig. 1 Schematic of the experimental setup for KrF excimer laser ablation of the glass.

	1
Parameters	Values
Wavelength (nm)	248
Repetition rate (Hz)	100
Pulse duration (ns)	3-7
Pulse energy (mJ)	1-20
Average power (mW)	300-5000
Scanning speed (mm/s)	1-25

Table 1: KrF excimer laser and beam specifications.

# 3. Results & discussion

In excimer lasers, there are three independent parameters that each have their own impact on the ablation: fluence (energy density), frequency (repetition rate), and translation speed (number of pulses per area). Since the effect of frequency is less significant (Liu et al. 2012) the fluence and number of pulses are considered in this paper. First of all, the optical transmittance of the glass was evaluated through UV/VIS spectroscopy (Fig. 2), which shows virtually all light will absorb at the wavelength of 248 nm.



Fig. 2 Optical transmittance of the soda-lime silicate glass before KrF excimer laser ablation. The inset image shows the glass substrate.

#### 3.1. Etch rate

A useful starting point for characterising the ablation of soda-lime glass is to measure the depth of material removed from the surface by each laser pulse, that is, the so-called etch rate per pulse. Fig. 3 shows the ablation rate for different fluences. For the tin side, a fluence of 400-500 mJ/cm<sup>2</sup> is the ablation threshold, i.e., the minimum energy required to induce atomic and molecular separation. The ablation rate started from 1 nm per pulse for fluence 500 mJ/cm<sup>2</sup> and one shot per area. This depth increases for the higher fluences. The maximum fluence used in this study is 1300 mJ/cm<sup>2</sup>, which is able to ablate around 50 nm by each pulse. One should be careful about using higher fluences as the quality of ablation may be adversely affected by heating the peripheral area, which leads to microcracks appearance.

#### 3.2. Linear relation between depth and number of passes

Another feature of the excimer laser ablation on soda-lime glass lies in the linear relation between the depth of ablation and the number of passes given in Fig. 4. It is shown that for a fluence of 800 mJ/cm<sup>2</sup>, by repeating the ablation on a specific line, the depth will increase in an almost linear way (R-squared  $\cong$  1). In other words, the ablation rate is independent of the number of pulses.

**CG** Challenging Glass 7



Fig. 3 Etch rates per laser pulse.

Fig. 4 Linear relation between depth and number of passes for fluence 800 mJ/cm<sup>2</sup>.

#### 3.3. Microholes

By controlling the parameter "number of pulses per area" which is related to the moving speed of the translation stage, we are able to induce microholes, at high speed, with a certain distance between them. Based on the mask and fluence, these microholes can have various shapes, dimensions, and depths. They are also useful to examine the roughness and uniformity of the ablation. Fig. 5 shows a 3D profile of separate pulses for the fluence of 800 mJ/cm<sup>2</sup> and one shot per area with five laser passes.



Fig. 5 3D view of laser ablation with separate pulses (the color scale bar represents the height profile in nm).

# 3.4. Depth profile and edge quality

Fig. 6 depicts the depth profile for three different passes obtained by the mechanical profilometer. The bottom roughness of lines increases for increasing depth, but it is still in a good range. It is worth mentioning that during ablation, laser energy pushed the glass to surroundings, creating a kind of accumulation at the edges (Liao et al. 2005). This phenomenon is also visible in the profile figures. It is good to know that the mechanical profilometers are not able to capture steep slopes because of the finite diameter of the probing needle. Therefore, sidewalls are more likely to be almost, but definitely not completely vertical after ablation (Babnik et al. 2013).

#### Experimental investigation into SLS glass surface modification using KrF excimer laser



Fig. 6 Ablation profile and top view of lines for different depths obtained by increasing the number of laser passes on one line.

#### 3.5. Tin side and air side

As mentioned before, all the results in this study refer to the tin side of the glass. We did experiments with the same laser parameters on both sides of soda-lime glass. However, the air side is not ablated at all while the depth of the line on the tin side is on the scale of micrometers. Probably more power is needed to reach the ablation threshold of the air side. The mechanical strength of the tin side is lower than that of the air side as during the manufacturing process, the tin side of the glass sheet passes over a number of solid roller surfaces, which introduce a population of subcritical cracks. However, this explanation could not be the main reason for our observation because during laser radiation, composition of the material plays the key role in the behaviour of ablation. One plausible explanation is that due to the contact with the tin bath, some diffusion of tin into the glass structure near the interface will occur. This diffusion will increase the refractive index of the tin side by approximately 0.2 to 0.3 (Synowicki et al. 2011) and may also

### **CG** Challenging Glass 7

increase the laser-material interaction in the UV spectrum. It is shown that some metals such as thin film of ZnO are used on soda-lime glass substrate and the excimer laser is employed as a deposition technique (Tsoutsouva et al. 2011; Winfield et al. 2007) because those metals have different absorption features in comparison to the glass. Therefore, the tin layer of the soda lime silica can act in a similar way, with the difference that this layer is integrated into the glass with a non-uniform distribution.

#### 4. Conclusions

In this paper, we presented a non-contact technique using KrF excimer laser (248 nm) to generate artificial scratches and defects with high accuracy on soda-lime silica glass. An ablation threshhold of 400-500 mJ/cm<sup>2</sup> is achieved for the tin side using this laser. By choosing the appropriate laser parameters, other types of damages such as chipping and plastic regions are avoided which makes it possible to only focus on the influence of certain surface damages with specific dimensions and cross-sections. In terms of accuracy, the depth from one nanometer to tens of micrometers is achievable using KrF excimer laser ablation on soda-lime glass. Easy-to-produce masks give us the advantage to generate various pulse shapes with different dimensions, e.g., 50 to 300  $\mu$ m width for square masks. In comparison to other (mechanical) methods, excimer lasers are highly accurate and have the potential to ablate different patterns, such as polylines, on the glass very fastly. However, in comparison to other lasers (CO2, pico- and femtosecond), there are some limitations that should be considered according to the required application. This point opens doors for further investigations on applying other types of laser on soda-lime glass to figure out the limitations and robustness of each laser.

#### 5. Acknowledgements

The authors gratefully acknowledge the contributions of Professor Jeroen Beeckman and Ph.D. student Xiangyu Xue (LCP team at Ghent University) to the UV/VIS spectroscopy.

#### 6. References

Ahsan, Md.S., Dewanda, F., Lee, M. S., Sekita, H., Sumiyoshi, T.: Formation of superhydrophobic soda-lime glass surface using femtosecond laser pulses. Appl. Surf. Sci. 265, 784-789 (2013)

Babnik, A., Petkovšek, R., Možina, J.: Influence of laser beam's image-plane position on geometry of through-holes in percussion-drilled glass using excimer laser. Maejo Int. J. Sci. Tecnol. 1(7), 48-59 (2013)

Basting, D., Marowsky, G. (Eds.): Excimer laser technology. Springer Science & Business Media (2005)

Ben-Yakar, A., Byer, R.L.: Femtosecond laser ablation properties of borosilicate glass. J. Appl. Phys. 96(9), 5316-5323 (2004)

Chen, Y.T., Ma, K.J., Zhou, J.G., Tseng, A.A.: Excimer laser ablation of glass-based arrayed microstructures for biomedical, mechanical, and optical applications. J. Laser Appl. 17(1), 38-46 (2005)

Datsiou, K.C., Overend, M.: Artificial ageing of glass with sand abrasion. Con. Build. Mat. 142, 536-551 (2017a)

Datsiou, K.C., Overend, M.: The strength of aged glass. Glass Struct. Eng. 2(2), 105-120 (2017b)

Dyer, P.E.: Excimer laser polymer ablation: twenty years on. Appl. Phys. A 77(2), 167-173 (2003)

Gattass, R.R., Mazur, E.: Femtosecond laser micromachining in transparent materials. Nat. Photonics 2(4), 219 (2008)

Glass Alliance Europe: Eurostat Data Year 2018, <u>https://www.glassallianceeurope.eu/images/cont/qa-reach-update-february-2018\_file.pdf</u> Accessed 15 January 2020

Gottmann, J., Hermans, M., Repiev, N., Ortmann, J.: Selective laser-induced etching of 3D precision quartz glass components for microfluidic applications—up-scaling of complexity and speed. Micromachines 8(4), 110 (2017)

Karstens, R., Gödecke, A., Prießner, A., Ihlemann, J.: Fabrication of 250-nm-hole arrays in glass and fused silica by UV laser ablation. Opt. Laser Technol. 83, 16-20 (2016)

Liao, Y.S., Chen, Y.T., Chao, C.L., Liu, Y.M.: Surface morphology and subsurface damaged layer of various glasses machined by 193-nm ArF excimer laser. Proc. SPIE 5715, Micromachining and Microfabrication Process Technology X (22 January 2005). doi: 10.1117/12.592034

Liu, K., NiCkolov, Z., Oh, J.: KrF excimer laser micromachining of MEMS materials: characterization and applications. J. Micromech. Microeng. 22(1), 015012 (2011)

Nieto, D., Arines, J., O'Connor, G.M., Flores-Arias, M.T.: Single-pulse laser ablation threshold of borosilicate, fused silica, sapphire, and sodalime glass for pulse widths of 500 fs, 10 ps, 20 ns. Appl. Opt. 54(29), 8596-8601 (2015)

Righini, G.C., Chiappini, A.: Glass optical waveguides: a review of fabrication techniques. Opt. Eng. 53(7), 071819 (2014)

Rudolph, T., Zimmer, K., Böhme, R., Ruthe, D.: Excimer laser-induced material modification to create nanometer high smooth patterns in glass using mask projection. Journal of Physics: Conference Series (Vol. 59, No. 1, p. 169). IOP Publishing (2007)

Schneider, J., Schula, S., Weinhold, W.P.: Characterisation of the scratch resistance of annealed and tempered architectural glass. Thin Solid Films 520(12), 4190-4198 (2012)

Van Steenberge, G., Geerinck, P., Van Put, S., Watté, J., Ottevaere, H., Thienpont, H., Van Daele, P.: Laser cleaving of glass fibers and glass fiber arrays. J. Lightwave Technol. 23(2), 609 (2005)

Synowicki, R.A., Johs, B.D., Martin, A.C.: Optical properties of soda-lime float glass from spectroscopic ellipsometry. Thin Solid Films 519(9), 2907-2913 (2011)

Tseng, A.A., Chen, Y.T., Chao, C.L., Ma, K.J., Chen, T.P.: Recent developments on microablation of glass materials using excimer lasers. Opt. Lasers Eng. 45(10), 975-992 (2007)

Tsoutsouva, M.G., Panagopoulos, C.N., Kompitsas, M.: Laser energy density, structure and properties of pulsed-laser deposited zinc oxide films. Appl. Surf. Sci. 257(14), 6314-6319 (2011)

Winfield, R.J., Koh, L.H.K., O'Brien, S., Crean, G.M.: Excimer laser processing of ZnO thin films prepared by the sol-gel process. Appl. Surf. Sci. 254(4), 855-858 (2007)

Zhang, J., Dong, W., Zhang, Y., Sheng, J.: KrF-excimer laser irradiation on the soda-lime silicate glass. Int. J. Hydrogen Energy 34(7), 3197-3200 (2009)



Challenging Glass 7 Conference on Architectural and Structural Applications of Glass Belis, Bos & Louter (Eds.), Ghent University, September 2020. ISBN 978-94-6366-296-3, www.challengingglass.com



PLATINUM SPONSORS



GOLD SPONSORS





Dow

ΕΛ<mark>ΣΤΜ</mark>ΛΝ

trosifol<sup>™</sup> world of interlayers

SILVER SPONSORS







Vitroplena structural glass solutions #letsglassifytheworld

ORGANISING PARTNERS





