Published in final edited form as:

Appl Phys Lett. 2008 ; 93(1): 011112-. doi:10.1063/1.2952832.

Novel morphologies and non-linear scaling of laser damage in glass by tightly-focused femtosecond pulses

Jeffrey F. Herbstman and Alan J. Hunt

Dept. of Biomedical Engineering, University of Michigan, Ann Arbor, MI 48109

Steven M. Yalisove

Dept. of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

Abstract

We examine the relationship between pulse energy and the morphology of damage in glass, produced by a tightly-focused femtosecond pulsed laser. For fluences up to three times that of threshold, an unexpected discontinuity in the scaling of damage size is caused by ejection of rings of material surrounding central damage that appear above a sharp threshold fluence. A mechanism for the production of these structures via thermal expansion and shockwave generation is proposed.

High numerical aperture (NA) femtosecond laser machining has proven to be an effective method for machining at the nanoscale, with varied applications including micro-electromechanical systems, biological sensors, and the generation of microfluidic structures in glass [1–5]. To achieve tight control of the scale and morphology of micron and submicron structures, knowledge of damage processes and characteristics close to threshold is essential. Near the threshold for damage it is possible to achieve highly repeatable damage with a diameter that is below the diffraction limit due to the highly nonlinear nature of ultrafast laser damage [6,7]. The underlying physical processes are not completely understood, but energy deposition has been attributed in varying degrees to avalanche ionization, multiphoton ionization and tunneling, under different material, incident wavelength, polarization, pulse duration and focusing conditions [8–13].

In this article, we present studies of laser damage morphology in Corning 0211 glass. When the laser is focused by a 0.65 NA objective lens, we observe a discontinuity in the relationship between damage diameter and fluence, corresponding to a change in the morphology of the damage. As the fluence increases past the discontinuity, the commonly considered damage mechanism of thermal vaporization and spallation of molten material is augmented by the ejection of grommet-shaped features. We characterize the formation of “grommets” and propose a mechanism for their origin.

A 600 fs directly diode pumped Nd:glass CPA laser (Intralase Corp., Irvine, CA) was frequency doubled using a KTP crystal to generate 527 nm light. Single pulses were then selected using a shutter and attenuated to fluences near the threshold for damage using a neutral density filter wheel. A polarizing cube was inserted in the beam path to linearly polarize the light, or in experiments using circularly polarization, a $\lambda/4$ waveplate was also inserted. The beam was then sent into an inverted microscope and focused using microscope objectives of different numerical apertures (NA) with the back aperture of each objective filled with light to obtain the full NA. Corning 0211 glass coverslips (Fisher Scientific, Waltham, MA) were used as targets and placed on a three-axis nanopositioning stage (Mad City Labs Inc. Madison, WI). The laser was focused through the coverslip to the far side, where a drop of water was placed on the sample to aid in debris removal. Once damaged, the samples were coated with carbon for observation using a scanning electron microscope (FEI Nova Nanolab, Hillsboro, OR).

The damage threshold was determined by firing single pulses at undamaged regions while making small changes in the height of the focus relative to the surface of the sample. The central hole is to first approximation presumed to be largest near the location where the focus and the surface coincide. The diameter measurements for different fluences were fit to the inverse of a Gaussian curve, with the diameter, $D = \sigma(\ln(I/\gamma))^{1/2}$, where I is the peak pulse fluence, σ and γ are fitting parameters, with γ giving the damage threshold, corresponding to the fluence where this curve predicts zero diameter damage [6].

As shown in Figure 1, when the laser was focused with an 0.65 NA objective, a clear discontinuity in the size of the entire damage feature occurs at $\sim 32 \text{ J/cm}^2$, below which sizes are dramatically reduced. As observed in previous work [6,14], damage consists of a deep central hole, surrounded by a region of variable morphology (e.g., figure 2). In contrast to the entire feature, the central hole size smoothly decreases with fluence, and the curve can be extrapolated down to the threshold for damage. The break in the curve describing feature size indicates an abrupt shift to a different damage mechanism, and closer examination of the damage spots reveals striking differences in the damage morphologies below and above the fluence at which the discontinuity occurs.

Damage observed at fluences close to threshold below the discontinuity exhibit a smooth central hole and raised outer ring as shown in Figure 2A & B. This damage is broadly similar to that seen in previous published work [6], but also exhibits, viewed from above, small bumps on the raised outer ring; this may be because, unlike the previous work, damage occurs at a water-glass interface. The presence of water at the damage site will rapidly quench heated material, potentially preventing the material forming the small bumps from being extruded entirely as seen in previously described spallation [14]. The morphology of damage at fluences above the size discontinuity shows markedly different damage characteristics, however. The clean central hole is still present, but additionally a thinner, flat, grommet-like structure is ejected from the surrounding material, and for fluences close to the size discontinuity, the grommets sometimes remain partially attached to the substrate (Figure 3A and B). The grommets have a relatively flat bottom, conical side walls, and a small lip near the surface of the glass. At a higher NA of 0.80, one can observe similar damage morphology (seen in Figure 3C) with removal of a central hole and an outer ring of material. Neither grommets nor removal of an outer ring of material were observed under tighter focusing conditions using a 1.3 NA objective.

The reproducible complexity of these features is intriguing, and the question arises as to how they are generated in a homogeneous, transparent solid. Where the laser comes to a focus at the back surface of the coverslip, an electron-hole plasma is generated via photoionization of carriers in the glass in regions where the intensity exceeds the sharp, highly non-linear threshold for damage [9,15]. The excited carriers then thermalize, transferring their energy to the lattice: this causes superheating of the glass, leading to ablation of the material [13]. The sharp, well-defined central hole formed at the fluences and NA examined is suggestive of this type of ablation, characterized by heating and vaporization, with additional possible contributions from self focusing or radiative drilling by short-wavelength Bremsstrahlung radiation caused by the formation of an electron-ion plasma [14–16]. Figure 4 shows characteristic damage for fluences above the size discontinuity (top), and near threshold (bottom). In Figure 4 A & C the tilt-view perspective reveals thread-like structures projecting perpendicularly from the sample surface in the region surrounding the central holes. These correspond to the small bumps on the raised outer rings in Figure 2A & B, which appear globular due to the viewing angle perpendicular to the sample plane (see 4C & D). The thread-like structures seen in the left row of damage in 4A and the top row in 4B also indicate that a liquid phase of glass was created along with the central hole during damage. These threads, 30–60 nm in diameter and less than $\sim 1 \mu\text{m}$ long, likely occur when jets of superheated molten material erupting from the central

hole are quenched by the water in contact with the glass surface. Closer to the damage threshold, blister-like structures (Figure 4C and D) are formed when the focus is slightly sub-surface. Such blistering has been observed in metals during fs laser ablation, and explained by formation of a layer of two-phase gas and liquid material that expands away from the layer of non ablated material below the skin depth [16,17], but this has not previously been observed in a homogeneous transparent dielectric. The blister-like structures that we observe suggest a similar mechanism occurs in glass under focusing conditions that cause a deposition of energy within a small depth range of the material during ablation [18]. As energy is absorbed, the temperature increases and vacancies generated by heating become more mobile. Simulations (in metals) show that these vacancies coalesce to form large voids in the material, while still leaving the surface layer intact [19]. Rapid heating over the sub-surface non-linear absorption depth leads to thermal expansion and a generation of a shockwave that pushes the surface of the glass outward, essentially creating a bubble of two-phase gas and molten material [14,16, 19,20]. However, the removal of grommets at fluences above the size discontinuity has not been previously observed, and shows the distinct damage character in the transparent dielectric. The grommets show less deformation than is seen in the glass threads described above. This indicates that though the central holes are generated by superheated ablation, the grommets may be below melting temperature when ejected, and are formed through a different process than the thermal vaporization and spallation that produces the central holes. For damage fluences in glass well above threshold, heavy absorption and damage at greater depth is expected as ionization occurs upstream of the focal region [18]. Thus when the beam waist is located at the surface, subsurface energy absorption will cause expansion both radially into areas with less deposited energy, and orthogonally to the surface, pushing the surface of the material outward, causing ejection of a solid layer if the deposited energy is sufficient to exceed the fracture strength of the glass. As seen in Figure 2, for fluences twice that of threshold, the high pressures that have been observed for tightly focused ultrafast damage (~ 10 TPa for sapphire [22]) can be large enough to totally remove the grommet. As the fluence is lowered, the grommet layer is raised, but not entirely removed, forming an attached structure as seen in Figures 3 and 4A/B.

Grommet ejection was observed when the laser was focused with 0.65 and 0.80 NA objectives, but not for 1.3 NA. This is consistent with subsurface absorption driving grommet ejection, as the larger Rayleigh lengths of the lower NA focusing conditions allows for energy to be deposited deeper below the surface focus, both in absolute terms and with respect to the beam waist. This subsurface energy deposition facilitates blister and subsequent grommet formation.

Additionally, the comparison of linearly polarized ablation and circularly polarized light indicates that for the ablation conditions tested, 0.65, 0.80 and 1.3 NA (only 0.65 and 0.80 shown here), there is no difference in threshold or morphology of damage. This extends, but is consistent with experimental observations of Joglekar et al. [8], and contrasts with a difference in threshold for circular and linear polarizations at shorter pulse durations [23]. As pointed out by Temnov et al. [23] these behaviors support theoretical calculations by Kaiser et al. [24], predicting that at longer pulse duration there should be little difference in damage thresholds.

In conclusion, while damage very near threshold at the surface of glass produces sharp, subdiffraction limit holes, at marginally higher fluences the damage features become complex. At fluences below the size discontinuity marking the onset of grommet formation, subsurface laser focus and energy absorption can generate blister-like structures. As the pulse fluence increases, increasing energy is absorbed upstream of the beam focus even when it is focused at the surface, and grommet shaped chunks are ejected as deeper energy deposition causes shockwave formation further from the surface. As incident pulse energy is increased these subsurface shockwaves cause the surface layer to be ejected, generating a corresponding ring

of removed material around the central hole. These findings show that for fs-laser damage in dielectrics, as the fluence is raised beyond threshold, energy dissipation processes quickly increase in complexity, and are central to determining the final damage morphology. Planned simulations and pump-probe experiments will lead us to a detailed understanding of the dynamic processes initiating blister and grommet formation.

References

1. Ke K, Hasselbrink EF, Hunt AJ. *Analytical Chemistry* 2005;77(16):5083–5088. [PubMed: 16097742]
2. Hwang DJ, Choi TY, Grigoropoulos CP. *Applied Physics a-Materials Science & Processing* 2004;79(3):605–612.
3. Marcinkevicius A, Juodkazis S, Watanabe M, Miwa M, Matsuo S, Misawa H, Nishii J. *Optics Letters* 2001;26(5):277–279. [PubMed: 18040300]
4. Schaffer CB, Brodeur A, Garcia JF, Mazur E. *Optics Letters* 2001;26(2):93–95. [PubMed: 18033517]
5. Uram JD, Ke K, Hunt AJ, Mayer M. Submicrometer pore-based characterization and quantification of antibody-virus interactions. *Small* 2006;2:967–972. [PubMed: 17193151]
6. Joglekar AP, Liu H, Spooner GJ, Meyhofer E, Mourou G, Hunt AJ. *Applied Physics B-Lasers and Optics* 2003;77(1):25–30.
7. Pronko PP, Dutta SK, Squier J, Rudd JV, Du D, Mourou G. *Optics Communications* 1995;114(1–2):106–110.
8. Joglekar AP, Liu HH, Meyhofer E, Mourou G, Hunt AJ. *Proceedings of the National Academy of Sciences of the United States of America* 2004;101(16):5856–5861. [PubMed: 15071188]
9. Bloembergen N. *Ieee Journal of Quantum Electronics* 1974;Qe10(3):375–386.
10. Vanstryland EW, Soileau MJ, Smirl AL, Williams WE. *Physical Review B* 1981;23(5):2144–2151.
11. Du D, Liu X, Squier J, Mourou G. *Applied Physics Letters* 1994;64(23):3071–3073.
12. Stuart BC, Feit MD, Herman S, Rubenchik AM, Shore BW, Perry MD. *Journal of the Optical Society of America B-Optical Physics* 1996;13(2):459–468.
13. Schaffer CB, Brodeur A, Mazur E. *Measurement Science & Technology* 2001;12(11):1784–1794.
14. Kudryshov S, Mourou G, Joglekar AP, Herbstman JF, Hunt AJ. *Applied Physics Letters* 2007;91(14):141111–141113.
15. Tien AC, Backus S, Kapteyn H, Murnane M, Mourou G. *Physical Review Letters* 1999;82(19):3883–3886.
16. Sokolowski-Tinten K, Bialkowski J, Cavalleri A, von der Linde D, Oparin A, Meyer-ter-Vehn J, Anisimov SI. *Physical Review Letters* 1998;81(1):224–227.
17. S.M. Yalisove, submitted to *Journal Of Applied Physics*
18. Schaffer CB, Jamison AO, Mazur E. *Applied Physics Letters* 2004;84(9):1441–1443.
19. Leveugle E, Ivanov DS, Zhigilei LV. *Applied Physics a-Materials Science & Processing* 2004;79(7):1643–1655.
20. K. Thornton and S.M. Yalisove, submitted to *Applied Physics Letters*
21. McDonald JP, Mistry VR, Ray KE, Yalisove SM, Nees JA, Moody NR. *Applied Physics Letters* 2006;88(15):Art
22. Juodkazis S, Nishimura K, Tanaka S, Misawa H, Gamaly EG, Luther-Davies B, Hallo L, Nicolai P, Tikhonchuk VT. *Physical Review Letters* 2006;96(16):4.
23. Temnov VV, Sokolowski-Tinten K, Zhou P, El-Khamhawy A, von der Linde D. *Physical Review Letters* 2006;97(23):Art
24. Kaiser A, Rethfeld B, Vicanek M, Simon G. *Physical Review B* 2000;61(17):711437–711450.

Figure 1.

0.65 NA damage in Corning 0211 glass for light that is circularly polarized (CP) and linearly polarized (LP). Because of an elliptical beam shape, both the major and minor axes were measured. Lines were fitted using the equation $D = \sigma(\ln(I/\gamma))^{1/2}$ to the major and minor axes data for the central holes.

Figure 2. Top down SEM images of 0.65 NA damage in Corning 0211 glass. A. CP 23 J/cm², B. LP 23 J/cm² C. 55 J/cm² D. 43 J/cm². Scale bar length on all images is 100 nm.

Figure 3.

A. 0.65 NA, LP, 40 J/cm². B. 0.65 NA, LP, 34 J/cm². Image taken 30° from the orthogonal to the surface – this shows a profile view of the grommet, with the flat bottom, conical side and lip at the surface. C. 0.80 NA, LP, 16 J/cm². Scale bar length is 100 nm.

Figure 4.

(A) Sideview and (B) Top view images of 40 J/cm^2 damage. (C) Sideview and (D) Topview images of damage near threshold (23 J/cm^2). The laser is focused deeper inside the glass surface for each spot in the direction that the arrows indicate, thus in (C) the top holes are focused deeper below the surface. In (A) and (B) the right/bottom row of damage occurs when the focus is near the surface, while the left/top row is focused deeper inside the material. The focus is scanned through the surface so that measurements of the damage threshold can be taken as close to the beam waist as possible. Images on the right side are taken orthogonally to the surface, images on the left side are taken at 55° (A) and 47° (C) degrees from the orthogonal. Scale Bar is $1 \mu\text{m}$.