

Initiation, Growth and Mitigation of UV Laser Induced Damage in Fused Silica

A.M. Rubenchik, M.D. Feit

This article was submitted to Laser-Matter Interaction-11, St. Petersburg, Russia, June 30-July 2, 2003

U.S. Department of Energy

June 10, 2003

Lawrence
Livermore
National
Laboratory

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy
And its contractors in paper from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-mail: reports@adonis.osti.gov

Available for the sale to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-mail: orders@ntis.fedworld.gov
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
<http://www.llnl.gov/tid/Library.html>

Initiation, Growth and Mitigation of UV Laser Induced Damage in Fused Silica

A.M. Rubenchik* and M.D. Feit

Lawrence Livermore National Laboratory, P.O. Box 808- L-491, Livermore, CA 94550

ABSTRACT

Laser damage of large fused silica optics initiates at imperfections. Possible initiation mechanisms are considered. We demonstrate that a model based on nanoparticle explosions is consistent with the observed initiation craters. Possible mechanisms for growth upon subsequent laser irradiation, including material modification and laser intensification, are discussed. Large aperture experiments indicate an exponential increase in damage size with number of laser shots. Physical processes associated with this growth and a qualitative explanation of self-accelerated growth is presented. Rapid growth necessitates damage growth mitigation techniques. Several possible mitigation techniques are mentioned, with special emphasis on CO₂ processing. Analysis of material evaporation, crack healing, and thermally induced stress are presented.

Keywords: laser damage, initiators, crater formation, mitigation

1. INTRODUCTION

The damage of optical elements is one of the main concerns for builders of large laser systems. The problems are especially severe for UV optics due to the more efficient interaction of high-energy photons with optical materials. Powerful laser light initiates a breakdown in fused silica and ionized material effectively absorbs laser radiation. This absorbed energy generates high temperatures and pressures and modifies and destroys the fused silica. The spatial extent of damage increases with repetitive pulses so that finally the optic becomes nonfunctional due to large obscurations or mechanical failure.

In the present paper, we discuss the physical phenomena associated with damage initiation and growth in fused silica, as well as methods to mitigate growth. Typically, laser damage studies deal with damage threshold [1]. However, the useful optics lifetime is determined mainly by the damage growth rate with repetitive pulses. Even the observable damage threshold is strongly influenced by damage growth during the laser pulse. As a result, much of our focus will be on damage growth.

First, we discuss the relations between intrinsic and defect-related damage. What kind of defects can initiate damage and how are they related to the polishing process? Laser absorption in defects and the surrounding matrix generates high pressure and temperature and produces a microexplosion. We will estimate the absorbed energy density and generated pressure and will evaluate the crater size, and extent of damage.

Damage sites continue to grow with repetitive pulses. We will discuss the growth mechanisms and experimental data on growth rate of damage spots. A qualitative explanation of the observed self-accelerated damage growth will be presented.

*Correspondence: Email: rubenchik1@llnl.gov; Telephone: 925-422-6131; Fax: 925-422-5099

Optics lifetime extension requires mitigation of damage growth. Among the few mitigation schemes explored, mitigation by CO₂ laser radiation looks most promising. We will analyze the physics of this mitigation process and will discuss the optimal mitigation schemes

2. INTRINSIC AND DEFECT-RELATED DAMAGE

Optical damage is produced by laser energy deposition in nominally transparent material. The photon energy is smaller than the bandgap and, hence, laser damage is intrinsically a nonlinear process. The physics of damage is evident for the case of ultra-short laser pulses[2]. If the laser pulse duration is shorter than the electron-phonon scattering time of about 10 ps, heated electrons have no time to transfer energy to the lattice during the laser pulse. Again because the pulse is so short, a large number of seed electrons is necessary for dielectric breakdown to occur. These can be produced by multiphoton ionization. Oscillating in an intense laser field, the electrons collide with atoms and are heated. When the electron energy exceeds the bandgap a new electron is produced by impact ionization and an electron avalanche is initiated. For short pulses, the only factor limiting development of the avalanche is the pulse duration.

To produce macroscopic damage, one must deposit a minimal energy per atom on the order of the lattice binding energy. Practically, one considers the optical material to be at the threshold for damage when the density of free electrons reaches the plasma critical density, 10^{21} cm⁻³ for 1 μm light. At the critical density, laser light absorption becomes very efficient, so the deposited density of laser energy is extremely high –sufficient to produce macroscopic damage. Ultimate manifestations of damage—material melting and ejection, crack formation, etc. takes a much longer time to form. Typically, they are produced well after the USLP pulse termination.

Because the processes determining threshold are intrinsic to the material, the threshold fluence for USLP is well defined, reproducible, and independent of spot size. The physics of damage initiation is much different for pulse durations well above 10 ps. In this case the energy electrons gain through collisions with atoms can be balanced by the energy transfer from electrons to the lattice. To keep an electron avalanche going the energy gain must overcome losses giving the criteria for avalanche existence [2]

$$\sigma E^2 > \gamma U_{ph} \quad (2.1)$$

Here E is the laser electric field and U_{ph} is the typical phonon energy. The electrical conductivity, σ, and the rate of energy transfer to the lattice, γ, are taken for electron energy near the bottom of the conduction band. The electron collisional rates and energy transfer rates in fused silica have been measured experimentally [3]; for 1 μm light the critical intensity I_d to establish the avalanche is estimated as 80 GW/cm² [2]. If we assume the Drude formula for the conductivity for 355 nm light, we find I_d=150 GW/cm². The above estimate is only a lower estimate for the intrinsic damage threshold of long pulses, since other possible energy losses are disregarded.

From Eq.(2.1), it follows that the intrinsic threshold fluence is proportional to pulse duration τ. This result is in strong disagreement with multiple experimental data [4] which demonstrates a scaling F_{th}~τ^x, 0.3<x<0.5. The intrinsic threshold fluence at 355nm for a 3 ns pulse according to the above estimate is about 450 J/cm², at least 50 times higher than the typical threshold fluence observed in experiments.

These facts indicate that the threshold for long pulses is actually determined by defects in the nominally transparent material. The occurrence of damage depends on the probability of finding suitable defects so that the damage probability now increases as the laser spot size increases. For small laser spots, the threshold fluence can be very high, close to the intrinsic threshold.

As a result of the probabilistic nature of defect caused damage, the threshold fluence is not an adequate characteristic of the material. A more useful characteristic, which can be assumed independent of spot size and is a function of the material only is the density of defects damaged at given fluence n(F) [5]. Typically, the dependence on fluence is a power law where k is typically ~8-12.

$$n(F)=bF^k \quad (2.2)$$

Materials are available for modern large optics in which the optical quality is high enough that bulk damage is either rare or completely absent compared to surface damage. Most of the observed damage is concentrated near the optics surface and, consequently, associated with defects arising from the polishing process. More prevalent and dangerous is the rear (exit) surface damage. For front side damage, plasma produced by the laser pulse shields the material and reduces material destruction. For rear side damage, the absorption zone moves toward the beam and laser energy is deposited inside the optical material. The confinement of the plasma produced increases the generated pressure and increases material destruction [6]. As a result, rear side damage is more visible and dangerous.

3. INITIATORS AND POLISHING PROCESS.

Damage in fused silica is typically localized on the surface and is related to the polishing process. Contributions to the damage initiators potentially include distributed point defects, residual micro-inclusions produced by the polishing process and microcracks generated during the polishing process. For high quality polishing, the thickness of material modified by polishing does not exceed 1 μm [7].

First, let us evaluate the role of point defects. To damage material one must heat it up to some high temperature T_0 . At high temperature, the bandgap collapses and the material starts to absorb laser light, thereby initiating a thermal explosion. The exact value of T_0 is not known, but the results are not sensitive to this value. We will use, for estimates, $T_0 \sim 2000^\circ\text{C}$. During a nanosecond pulse, thermal conduction is negligible and the local temperature increase can be estimated from the energy balance.

$$\rho c T = \alpha F$$

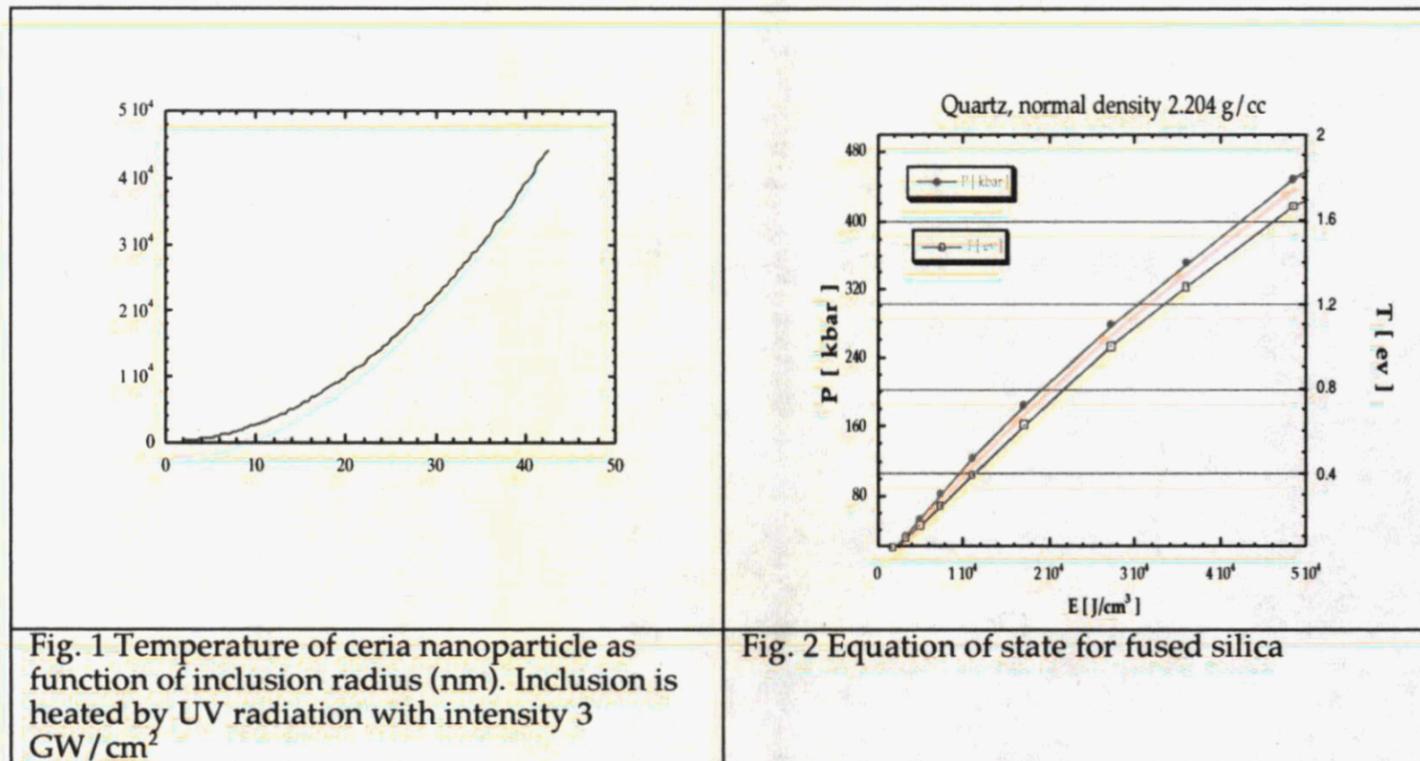
For fluence $F=5 \text{ J/cm}^2$, to increase temperature by T_0 the absorption coefficient α must be larger than 300 cm^{-1} . For homogeneously distributed defects the susceptible parts of material must have a high absorption and must look black. Fused silica can have a variety of point defects, see e.g. the review [8]. To estimate the number of defects needed we suppose that every defect can absorb 2 eV of energy. This corresponds, for example, to non-bridging oxygen centers (NBOC). It is easy to see that to heat the material up to $T \sim T_0$ the density of defects n must be about 10^{22} cm^{-3} . This density is too high to be real, and we can conclude that distributed point defects can not be responsible for the observable damage. It is realistic if the defects are combined into small clusters or if some small inclusions are present in the material. Such an absorber can be, for example, ceria microparticles, which are commonly used in the polishing process. The energy absorbed by a small particle with radius a much smaller than the laser wavelength is $Q = \alpha \pi a^2$. The absorption efficiency $\alpha = \sigma / \pi a^2$ is given by expression [9]

$$\alpha = \frac{12n\omega a}{c} \text{Im} \left[-\frac{n^2}{\epsilon + 2n^2} - \frac{1}{6} + \frac{1}{2(ka)^2} - \frac{\text{Cot}(ka)}{2ka} \right] \approx -\frac{12n\omega a}{c} \text{Im} \frac{n^2}{\epsilon + 2n^2} \quad (3.1)$$

Here $n=1.5$ is the refractive index of the glass matrix and ϵ is the dielectric constant of the particle. The ceria particle refractive index at wavelength 355 nm is $\sqrt{\epsilon} = 2 + 0.2i$ [10]. For this case $\alpha = 0.45\omega a / c = 0.008a \text{ nm}^{-1}$. Due to the small particle size the temperature distribution can be treated as stationary. For linear thermal conduction, the temperature T_0 near the particle surface is given by the formula

$$T_0 = \frac{\alpha a}{4\kappa} \quad (3.2)$$

A plot of the ceria particle temperature as a function of the inclusion radius a is presented in Fig.1 for laser intensity 3 GW/cm^2 and thermal conductivity $\kappa = 0.02 \text{ W/cmK}$. The temperature dependence of the thermal conductivity doesn't change the situation qualitatively even for very small inclusions, and particles a few tens of nanometers in size can initiate damage in fused silica.



The idea of nanoparticles being the main cause for damage initiations has been discussed in many publications; see e.g.[11]. At first glance, the idea is inconsistent with experiments. From Eq.(3.2) one can see that the threshold fluence for a fixed size particle is expected to be proportional to the pulse duration. As we discussed above, the experimentally observed threshold fluence varies with pulse duration as a fractional power between 0.3 and 0.5 [4]. The contradiction can be resolved if we assume that the material has an ensemble of microinclusions of various sizes. It is possible to show that for a given pulse duration, the most dangerous inclusions are of a size comparable to the thermal diffusion length $l \sim \sqrt{D\tau}$ [12,13]. Detailed calculations result in pulselength dependence of threshold consistent with experiment [13].

Damage initiation is often associated with microcracks. We can present several arguments to suggest why this is so. First, microcracks can effectively trap inclusions, thereby protecting them during the cleaning procedure. Second, microcracks can produce field enhancements both as a result of electrostatic enhancement originally pointed out by Blombergen [14] and by interference of light reflected and scattered by cracks [15]. Also, the presence of cracks weakens the material. The deposition of the same amount of energy in the weakened material can produce damage of a greater extent and, hence, more noticeable. Experiments by Hamza et al with artificial cracks demonstrate a direct correlation between the drop in damage threshold and the magnitude of material cracking [16]. Consequently, an improvement in the polishing procedure, e.g., reducing the number of microcracks by gentler polishing, can reduce the initiator density substantially [17].

4. THERMAL EXPLOSION AND FIREBALL GROWTH

When the temperature around the inclusion reaches a critical value, a thermal explosion takes place. This involves the rapid expansion of the heated region into the glass, which is then ionized. It occurs because the plasma produced by the initially absorbed light radiates UV, which is strongly absorbed in the matrix resulting in heating and an increase in the absorption coefficient of the glass. The situation is very similar to a laser-supported ionization wave, with the main difference being that for a small inclusion the ionization front is spherically symmetric. In the following, we assume the Drude model for the dielectric coefficient of the plasma:

$$\varepsilon = 1 - \frac{n_e}{n_c \left(1 + \frac{i\nu}{\omega}\right)} \approx -\frac{n_e}{n_c} \left(1 - \frac{i\nu}{\omega}\right) \quad (4.1)$$

where n_e is the electron density, n_c is the critical density, and ν is the electron collision frequency.

Consider the situation having the plasma density in a fireball close to critical and the electron scattering rate smaller than the light frequency. We assume that most of the absorbed energy is spent ionizing the material and only small part of the absorbed energy is spent heating the material. The rate of growth of the plasma ball can be estimated from energy balance:

$$n_e I_0 4\pi a^2 \frac{da}{dt} = \sigma I(t) \quad (4.2)$$

Here I_0 is the ionization potential and n_c is the electron density. If one uses only the first term in Eq (3.1) for the absorption cross section, the radius of the fireball grows exponentially: $a = a(0) e^{x \mu G}$, where the growth factor G is given by

$$G = 10 \frac{F\omega}{n I_0 c} \operatorname{Im} \frac{1}{\varepsilon + 2} \quad (4.3)$$

The growth factor is independent of pulse duration and is determined by the fluence only. Let us discuss the value of the electron density in the plasma fireball. The plasma temperature in this very dense plasma cannot be higher than a few eV due to huge radiation losses. Experimental data of Carr et al [18] indicates a plasma temperature below 1 eV for fluences of about 10 J/cm². The equilibrium electron density at this temperature, determined from the Saha formula, is much smaller than the critical density and cannot provide the effective absorption.

The additional non-equilibrium ionization is produced by laser radiation. Free electrons oscillate in the laser electric field, gain energy due to collisions and produce new free electrons. The ionization rate by electron impact is given by

$$\frac{dn_e}{dt} = \alpha I n_e \quad (4.4)$$

We will take the coefficient α from ref[2], for fused silica $\alpha \sim 10 \text{ cm}^2/\text{nscGW}$. One can see from the arguments presented in ref[2] that α for the dense cold plasma must have the same order of magnitude. For laser intensity $I = 2 \text{ GW/cm}^2$, the ionization time is about 50 ps. We see that the impact ionization can easily increase the electron concentration during the pulse up to the critical value. Electron density cannot greatly exceed the critical density value. In this case, the absorption depth becomes smaller than the fireball radius and the absorption efficiency drops. For absorption at 3 ω , a solid state density even about ten times critical, ionization potential of 10 eV, fluence F of 10 J/cm², and scattering rate 0.5 of the optical frequency, the growth factor G (4.3) is about 10. Taking into account the growth of absorptivity with increase of radius, we can say that if plasma formation starts, the plasma ball will rapidly grow to a size for which $ka > 1$, $k = \frac{\omega}{c} \sqrt{\varepsilon}$. In this case $ka \gg 1$ while $k_0 a \ll 1$ the absorption cross-section is

$$\sigma = 6\pi a^2 n \operatorname{Re} \frac{1}{\sqrt{\varepsilon}} \quad (4.5)$$

which grows only proportionally to the geometric area. Using Eq. (4.5) for the absorption cross-section, we have

$$a(t) = 3.5 \text{Re} \frac{1}{\sqrt{\epsilon}} \frac{\int_{-\infty}^t I(t) dt}{nI_0} \quad (4.6)$$

The plasma sphere radius at the end of the pulse is seen to be

$$a = 3.5 \text{Re} \frac{1}{\sqrt{\epsilon}} \frac{F}{nI_0} \quad (4.7)$$

where F is the fluence and I_0 the ionization energy.

For the parameters used above, this radius a is about 500 nm, comparable with the size of wavelength. Now the strongly absorptive plasma ball shields its rear surface. There is no simple description for fireball absorption; Mie theory must be used to calculate it [19]. The plasma can expand toward the laser light from the front surface like the laser-supported detonation wave (LSDW). But the lateral losses due to thermal conduction and light scattering arrest the LSDW propagation. As a result the fireball doesn't grow larger than the laser wavelength.

We argued above that absorption of laser light by small particles can produce a plasma fireball with size comparable to the laser radiation wavelength λ . Such a fireball of size, a, will absorb almost all incident energy, so the energy of the fireball can be estimated as $E \sim F\pi\lambda^2$, where F is the laser fluence. The energy density in the fireball is about $F/4/3\lambda$. For a fluence of $F=5 \text{ J/cm}^2$ and $\lambda \sim 350 \text{ nm}$, the total deposited energy is about 20 nJ and the energy density is $\sim 110 \text{ kJ/cm}^3$, approximately 10 times larger than the typical evaporation energy density E_e .

One can obtain a better estimate for the energy density in the fireball from a fireball temperature measurement [18]. It was found that the temperature of the fireball 10 ns after the pulse is about 0.5 eV. Due to the confinement by the surrounding material, the density in fireball is the same as in solid state. From the equation of state for fused silica presented in Fig.(2), one can find the energy density in the fireball and the generated pressure. The above temperature corresponds to a pressure about 150 kbar and energy density 15 kJ/cm^3 , which is roughly consistent with estimate presented above taking into account that assumption of total energy absorption in the fireball is clearly an overestimate.

5. CRATER FORMATION

After the pulse termination the absorbed energy is concentrated in a small fireball with energy density well above the evaporation energy. It means that the damage extent is determined by the total energy of the fireball, not the fireball size and structure. The problem of describing laser damage crater formation is similar to that for underground explosions or meteorite impacts, and we will use some of the ideas developed there [20].

The microexplosion creates a strong shock wave. After this shock wave passes, the resulting crushed material can be described as an incompressible liquid. The strength of the material is taken into account by assuming that the region of crushed material is bounded by the point at which the material velocity v becomes smaller than a critical velocity, c. This velocity, c, can be estimated by $\rho c^2 = G$ where G is the characteristic "strength" of the material. For example, the compressive strength of fused silica, $G=1 \text{ GPa}$, corresponds to velocity $c=670 \text{ m/s}$, much less than the sound speed 5.8 km/s .

Before presenting specific results, we make some general comments based on scaling. The radius, R, of a crater produced by an explosion with released energy E, buried a distance h beneath the surface, is determined by E, h, G and ρ . The most general relation between these parameters is of the form

$$R = hf(E/Gh^3) \quad (5.1)$$

where f is a function which needs to be determined from modeling or experimental data. Thus, for craters with the same R/h ratio, the crater size will be proportional to $E^{1/3}$. The scaling law actually observed in experiments with explosives gives an index value between $1/3$ and $1/4$ [20,21]. Fig.(3) adapted from [19] demonstrates that the scaling works over 4 orders of magnitude in explosion energy. The deviation from $E^{1/3}$ scaling in explosion craters for high-energy explosion is due to the effect of gravity which is insignificant for laser damage. Formula (5.1) indicates also the role of material strength, to produce the same crater in weaker material one needs to deposit less energy. We recently developed a simple hydrodynamic description of crater formation [22], which fits well the experimental data (see Fig.(3)). It was shown that for an explosion with fixed energy E , there is a maximal burial depth h_d for which a surface crater is formed and a depth h_m for which the resulting crater has maximum size,

$$h_m = \frac{h_d}{3^{3/4}} \approx 0.44h_d \quad (5.2)$$

Crater radius as function of charge depth is given by the expression [22]

$$R^2 = h^2 (h_d^{4/3} - h^{4/3}) \quad (5.3)$$

The maximal crater radius is given by

$$R_m = \sqrt{2}h_m \approx 0.6h_d \quad (5.4)$$

At high explosion energy or for shallow absorbers, the crater radius increases with burial depth as $h^{1/3}$

$$R = (h_d^2 h)^{1/3} \quad (5.5)$$

In Fig. 3 we compare the scaling predicted by Eq.(4.3) with experimental data for strong explosions. The value of the maximum depth for which the crater would just open, was used as the only adjustable parameter. We see good correlation with the experimental data.

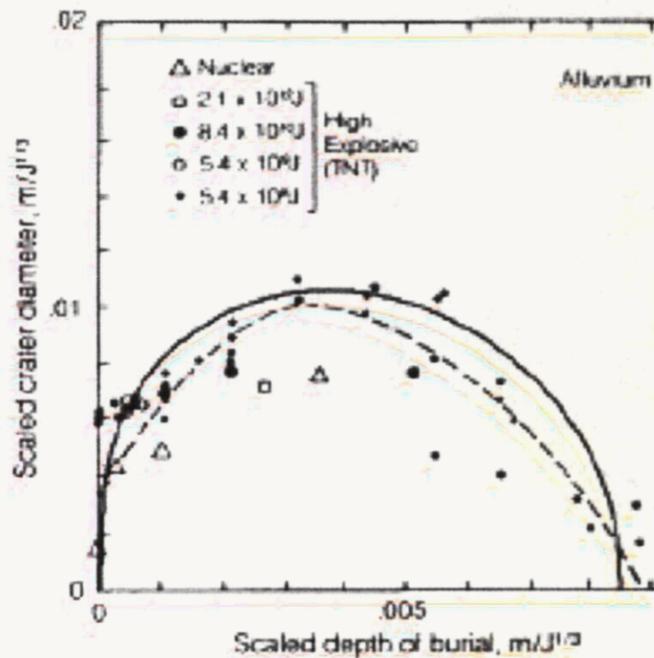


Fig. 3 Explosion crater diameter vs. depth of burial in alluvium at the Nevada Test Site [21]. This figure exemplifies $E^{1/3}$ scaling and indicates the importance of the depth of burial for explosions. The dashed line, drawn by the author, is to aid the eye. The solid line is the plot of crater diameter given by theory.

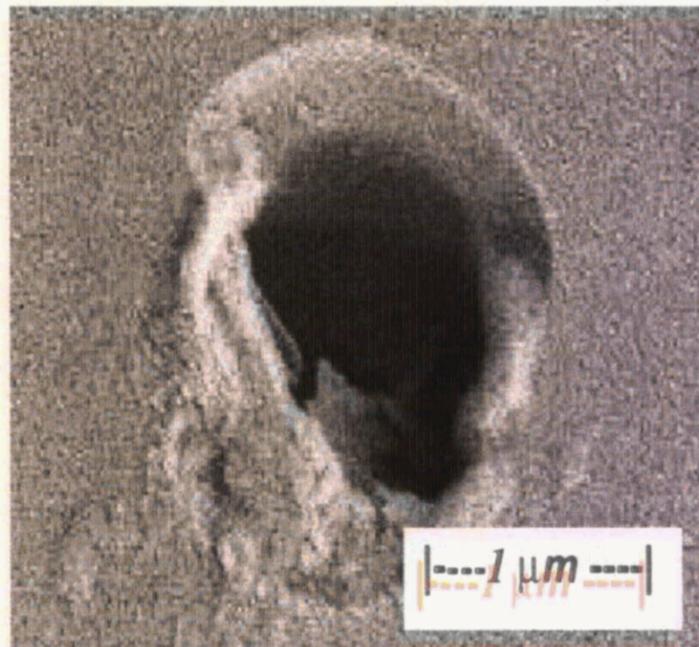


Fig. 4 Damage crater initiated at low fluence

We can derive an idea of the size of the various terms above for the laser damage regime by considering some typical values for fused silica. We take the laser fluence of 5 J/cm^2 , and the absorbed energy $F\pi\lambda^2 \sim 15 \text{ nJ}$. We can also apply the experimental explosion data from Fig. (3) laser damage regime. To use these data, we must take into account that glass is much stronger than alluvium, with $G \sim 1 \text{ GPa}$, so we rescale the energy according to Eq.(5.1). Taking the experimental value of 2 MPa for the strength of fractured rocks [20], we get $h_d \sim 2 \text{ }\mu\text{m}$ and $R_m \sim 1.2 \text{ }\mu\text{m}$. The usual estimate of the thickness of the layer modified by polishing process is $< 1 \text{ }\mu\text{m}$, and it means all craters must be wide open.

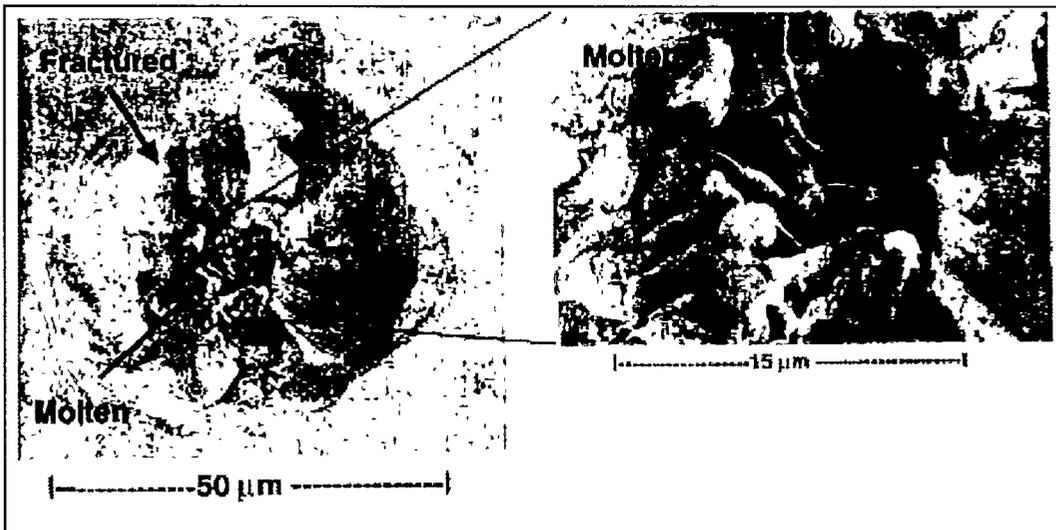


Fig. 5 Crater produced by 45 J/cm^2 pulse. SEM images show molten central region surrounded by fractured material.[22]

This estimate is consistent with size of crater presented in Fig. 4, produced by a low fluence shot. The situation is different for damage produced at high fluences. The image of such a crater is presented in Fig. 5 One can see that the size of the crater is $20\text{-}30 \text{ }\mu\text{m}$, inconsistent with above estimates. Also, the morphology of the craters are different, the material around the crater produced by the powerful shot is cracked and modified. The discrepancy can be explained by the modification of fused silica by the strong shockwave.

It has been found experimentally that propagation of strong shocks in glass are followed by a slower moving "failure wave" [23]. After passage of the failure wave, the glass, under the effect of high pressure, is densified, modified in structure, lower strength and crushed. This process occurs more rapidly than excavation by hydrodynamic motion. Thus, for high laser intensities it would be natural to use the strength of crushed rock of 2 MPa in the estimate above. In this case, the maximum crater diameter at 45 J/cm^2 increases to about $40 \text{ }\mu\text{m}$, which agrees with experiment.

This suggests a practical formula for estimates of crater size. If we estimate the energy absorbed by the fireball as $E = F\pi\lambda^2$ and use the experimental data from Fig.(3), the crater diameter can be given as

$$d = \left(F\pi\lambda^2 \frac{G_a}{G} \right)^{1/3} \quad (5.6)$$

Here, all lengths are in cm, F is in J/cm^2 , G is the effective strength of silica, and G_a is the strength of alluvium. It is not clear now at what fluence the transition from one type of crater to another takes place. Is the boundary sensitive to pulse duration and absorber size? We will argue later that this question is important for estimates of the damage growth by the repetitive pulses.

Self-consistent, comprehensive modeling of crater formation must include various physical effects including the laser interaction with plasma fireball, fireball expansion, phase transformations in surrounding materials, the

flow of crushed material, etc. The existent modeling includes only a part of the important physics [11,24]. Nevertheless, the modeling is able to catch some essential features of crater formation.

Experimentally, the possibility of initiating damage at a nanoparticle was demonstrated in experiments [25,16]. In the experiments of ref.[25] tiny gold nanoparticles with diameters about 5 nm were attached to the surface of SiO₂ material and then were coated by 60 nm of deposited SiO₂. The material was irradiated by 351 nm pulses with pulse duration 0.5 nsec. The damage was observed as a formation of wide open craters with threshold about 1.2 J/cm². According to our estimate Eq.(3.2) the temperature on the surface of the gold nanoparticle must reach 3200°C, a temperature sufficient to start the thermal explosion. The crater size is smaller than predicted by Eq.(4.6); for a fluence of 7.2 J/cm² the lateral crater size was slightly bigger than 200 nm. Probably the small burial depth (60 nm) can explain it. According to Eq.(4.5), the lateral size is predicted to be about 350 nm, not very far from experiment. An additional factor can be the short pulse duration, which can affect the fireball growth. In the experiments of ref.[16] the nanoparticles were larger (60nm) and the burial depth was 500 nm. The final craters were about 1 μm in size, in agreement with the above arguments. The experiments with craters formed which are many times larger than the initial nanoparticle confirms the pattern of damage induced by nanoparticles presented above-formation and growth of a plasma fireball, with storage of enough energy to produce the observed crater.

6. DAMAGE GROWTH

The density of defects in modern optics is very low. So the appearance of a few small craters doesn't appreciably affect optic performance. Unfortunately, the damage spots grow larger with consequent shots and finally the obscuration exceeds a specification limit or physical integrity will be destroyed. To estimate the useful optics lifetime, one must know the damage growth rate and factors affecting the growth. The key question to answer is why does the damage spot grow at all?

To have any modification of the damaged site by a new pulse, the absorption of laser radiation must take place. The material around the crater can be crushed, and strongly scatter light, but microscopic pieces of the original material has the same bandgap as the bulk material and are unable to absorb the light. We still are very far from a full understanding of light interaction with the damaged material. Below we list several mechanisms we think most likely to explain the absorption in the damage spot.

Heating of fused silica stimulates the loss of oxygen. Oxygen depleted material can efficiently absorb UV radiation. In Fig.(6) we show the absorption coefficient for SiO_x material as a function of oxygen depletion. One can see that oxygen depletion results in high absorption efficiency. For example, the absorption of a 3 ns 5 J/cm² laser pulse in a 1 nm film of SiO embedded in a glass matrix produces a local temperature increase over 5000K. This effect suggests an explanation for the difference in damage growth in vacuum and air observed in experiments. It is easier for the oxygen to escape in vacuum so the damaged material must be more absorptive. Unfortunately, to date, there is no conclusive evidence that the damage is related to oxygen deficiency in damage spots [26]. The experiment of ref[26] did not find a direct relation between the formation of sub-stoichiometric silica on the surface and an increase in damage vulnerability.

The high pressure generated by laser light absorption modifies fused silica [23]. Material is densified, and the structure changes. For example, the number of 3 and 4 member rings increases. The electronic structure also changes and the modified material can start to absorb UV. A layer of 20% densified material with thickness of a few microns was found in damaged spots by J.Wong et al [28]. Recently, an attempt to model this effect from first principles was carried out by A. Kubota et al [29]. Modification of fused silica due to the damage-induced shock wave was studied using the molecular dynamics method. Densification on the level of 20%, consistent with experiment, was found. After that the electronic structure of the modified material was modeled and a shift of the absorption edge toward the longwave part of the spectrum was found (see Fig.7). The calculated shift is large enough to greatly enhance two photon absorption. This initial result demonstrates at least the possibility of strong absorption in the shock-modified material.

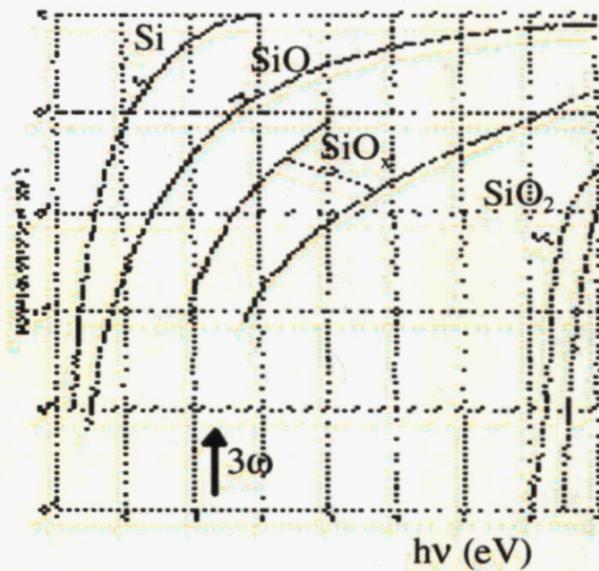


Fig. 6 The absorption in oxygen depleted material [27]. Absorption coefficient vs. photon energy for Si, SiO, SiO_x (x~1.5) and SiO₂

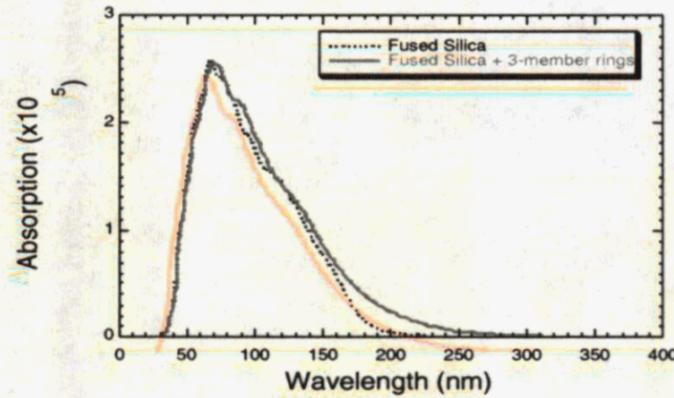


Fig. 7 : Modeling of electronic structure of modified material indicates the absorption increase in comparison with initial fused silica

Finally, small particles in the crushed material in damage spots can strongly scatter light. The interference of the scattered light produces local intensity spikes where breakdown can take place, igniting plasma and producing the enhanced absorption.

Scattering results in fast randomization of the radiation field. For a random Gaussian wave field with mean intensity I_0 the probability to have intensity I is

$$P(I) = \frac{e^{-I/I_0}}{I_0} \quad (6.1)$$

Typically, the density of defects damaged at intensity I , $d(I)$ are given by power distribution

$$d(I) = AI^n, \quad n \sim 10$$

Averaging density of defects over distribution (6.1) we have

$$\langle d(I) \rangle = A \langle I^n \rangle = An! I_0^n = n! \langle d(I_0) \rangle$$

We see that the probability to have damage greatly increases ($n!$ times) in comparison with coherent radiation at the mean intensity. This means that at high intensities at damage spot we must expect the generation of multiple absorption spots forming an extended strongly absorbing plasma.

Probably all of these mechanisms are important and manifest, to some degree, in reality. Damage spots on the rear side of the optic are particularly dangerous. In this case, light absorption in the damage spot creates plasma inside the material. Light absorption in the plasma initiates a laser supported detonation wave propagating back toward the laser beam. The deposition of energy inside the material greatly increases (3-6 times) the pressure in comparison with front surface damage [6] because of confinement. Generated shocks modify and crush the material and initiate cracks. Cracks continue growing long after pulse termination. There is no reliable way at present to theoretically describe the variety of physical phenomena operating on very different temporal and spatial scales. So the only complete way to study the damage growth at present is by experiment.

The experiments on damage growth carried out at LLNL revealed a reproducible and consistent pattern of damage growth (see Fig.8 and Fig.9) [30].

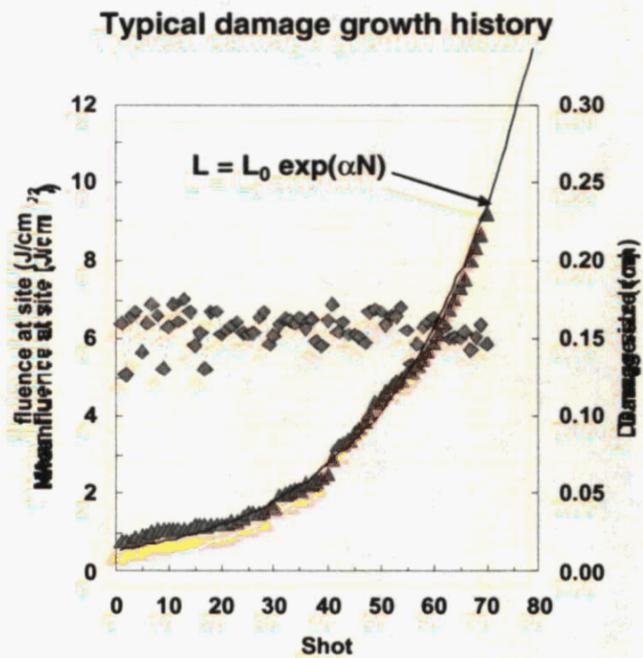


Fig. 8 Growth of damage spot with repetitive pulses

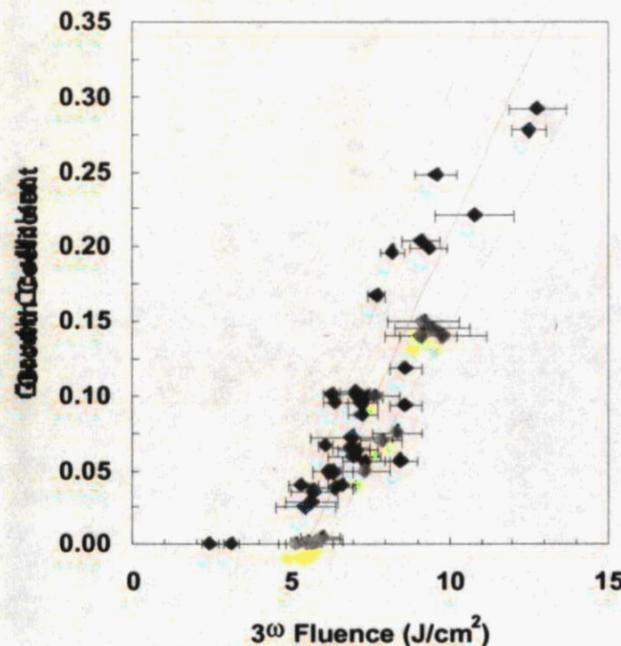


Fig. 9 Growth coefficient scales linearly with fluence above a threshold

The transverse size of the damage spot increases with the number of pulses in an accelerated way very well approximated by an exponential function

$$L = L_0 e^{\alpha N}$$

Damage growth has a threshold (Fig. 9). No damage growth occurs for fluences below about 5.5 J/cm^2 ; for higher fluences the growth coefficient scales linearly with laser fluences. This data can be approximated by formula where the fluence is in J/cm^2 .

$$\alpha = 0.047(F - F_{th}); F_{th} = 5.5 \text{ J/cm}^2 \quad (6.2)$$

Let us try to explain, at least, qualitatively, the observed results. Visual observations at the developed stage of growth show that the spot size grows mainly by the development of conical cracks on the periphery of the damage spot. To open a crack of length l one must apply the stress $\sigma = K/\sqrt{l}$, where K is the toughness of the material. $K = 0.75 \text{ MPa m}^{1/2}$ for fused silica. The laser energy absorption in the initially damaged zone produces some residual pressure P , e.g., due to thermal expansion of the heated material. This pressure produces hoop stresses outside the damage spot that open the crack. The extent of the stress zone increases with the increase of the damage spot size. We see that with increased spot size, it is easier to open the crack and the opened cracks are longer. This is consistent with observed accelerated growth.

If the scale of the damage zone is R the stresses decay outside as $P(R/a)^3$, the crack will grow to the size when stress becomes equal K/\sqrt{a} or

$$a = R^{6/5} (P/K)^{2/5}$$

If $a > R$ the increase of R after one shot will be which is close to exponential growth.

$$dR/dN = a = R^{6/5} (P/K)^{2/5}$$

The above estimates show that the optics lifetime is extremely sensitive to the structure of the initial crater. If the initial crater is a large and it is surrounded by weakened material, it will be easy to start a new crack and damage will grow exponentially. If the initial crater is small and the material around it is not damaged, it is difficult to create a new crack and rapid damage growth can be postponed.

It must be emphasized again that modern high quality optics have a very low density of defects, and it is very difficult to find and to grow damage site initiated at more typical laser operating fluences of 10 J/cm^2 . For this reason, the initial damage in the experiments [30] was initiated at high fluence, typically at 45 J/cm^2 . The crater produced at such fluence is shown in Fig. (5) and must be very susceptible to growth. As a result, the initial stage of growth for craters initiated closer to 10 J/cm^2 may be much longer than in these particular experiments. In the real situation, various initiators produce different craters, and not all may grow at 5.5 J/cm^2 . But when exponential growth starts, the optics become nonfunctional after $1/\alpha$ shots.

7. GROWTH MITIGATION.

It appears impossible in large-aperture laser systems to escape laser damage. Even initially perfect optics can be damaged due to mishandling or contamination during operation. For a system operating with peak fluences above 5 J/cm^2 , some scheme of damage mitigation must be found to extend optics lifetime. From our previous discussion it is clear that for damage mitigation, the modified material must be removed from the damage spot and cracks must be removed or healed.

A few different methods of mitigation were proposed and tested [31]. The most promising now appears to be mitigation by CO_2 radiation [31]. Fused silica absorbs 85% of the incident CO_2 radiation on the scale few μm . Local heating increases the surface temperature and evaporates the material. Heated up to high temperature material is revitrified and heals the microcracks. Treatment replaces the damage spot with a smooth Gaussian-shaped pit.

Let us discuss optimal parameters for damage spot mitigation. We will suppose that at high enough temperature the modified material will be transformed to the initial fused silica. Due to the extremely high viscosity of fused silica the most sensitive part of mitigation process is the crack healing. We will see that the temperature required for crack healing is so high that substantial evaporation is inevitable.

The steady state evaporation rate (velocity of evaporation front) is very sensitive to the surface temperature [32]

$$V = \frac{dZ}{dt} = V_0 e^{-\frac{U}{T_s}}, \quad (7.1)$$

Here U is the latent heat of evaporation per atom, 3.6 eV for glass, and T_s is the surface temperature. The constant V_0 is determined by the kinetics of the flow in the Knudsen layer near the surface, but its value is on the order of the sound speed in the condensed phase [32]. For validity of Eq.(7.1), it is clear that the laser pulse duration must be longer than the time for onset of steady temperature distribution: $a^2/4D$, where a is the damage spot radius and D is the thermal diffusivity. If the pulse is shorter than this time, a high evaporation rate takes place only in the end of the pulse and the removal rate will be sensitive to the pulse shape. In the steady state regime the removal rate is less sensitive to the pulse details.

Also, for the short pulse the high temperature zone has no time to diffuse deep enough to heal the cracks; in the steady state regime temperature is high in a thick enough layer to anneal the damaged material. Due to the high sensitivity of evaporation rate to the temperature of the surface it is difficult to find the optimal laser power. Low power will not remove any material; high power will produce a huge hole. A plot of the evaporation rate as a function of laser beam power is presented in Fig.10.

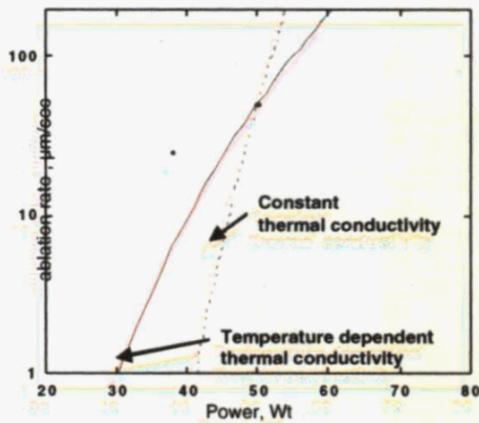


Fig. 10 Comparison of ablation rates calculated with linear (dash line) and nonlinear thermal transport. Dots are experimental values. Laser spot diameter-2mm.

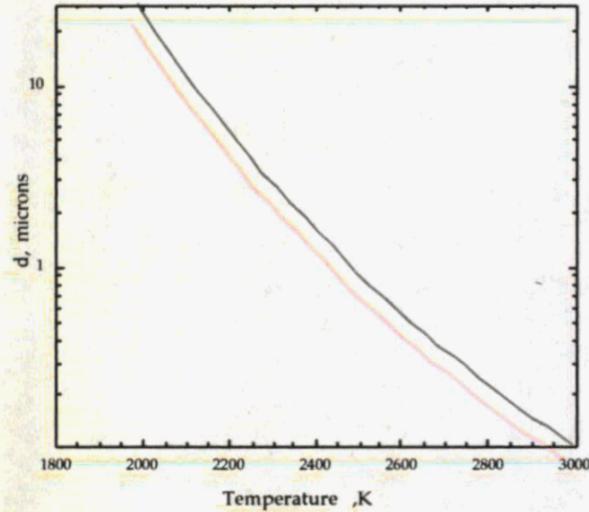


Fig. 11 The amount of material ablated during the crack healing procedure

The dotted line represents calculations done assuming temperature independent thermal conductivity. We see that the power dependence of the ablation rate is very steep and it means that damage spot processing is very sensitive to variation of laser parameters. Fortunately, the thermal transport is strongly nonlinear. The effective glass thermal conductivity increases with temperature and after $T \sim 800 \text{ K}$ is determined mainly by radiation transport. For thermal conduction we used the interpolation formula

$$\chi(T) = \chi_0 + \beta T^3 = 0.01(1 + 1.7 \cdot 10^{-9} T^3) (\text{W/cmK}) \quad (7.2)$$

The coefficient β is determined from experimental data, $\kappa \sim 0.04 \text{ W/cmK}$ at $T = 1200 \text{ K}$ [33]. One can see that nonlinearity of thermal conduction makes the ablation rate more flat and less susceptible to the variation of laser parameters. Including the effect of nonlinearity on thermal transport brings the modeling results closer to experiment, but the difference is still large. The reason is that the ablation rate is extremely sensitive to surface temperature and the absence of detailed information about thermal transport limits modeling accuracy.

The ablation rate observed in an experiment is determined exactly by the surface temperature. For an ablation rate of $50 \mu\text{m/s}$, the surface temperature T_s is 2245 K , and even a 5% change of temperature changes the ablation rate more than 2 times.

The calculation and experimental data are presented for one value of beam radius a . It is easy to show that the ablation rate is a function of the ratio P/a only for any nonlinearity of thermal conduction. It means that the curve in Fig.(10) is a universal one; it can be measured for some fixed beam radius and then rescaled to any interesting situation.

The high temperature induced by infrared radiation not only evaporates the material but reduces the viscosity of fused silica so surface tension now is able to close the cracks, thereby annealing the material and increasing the optical strength. The increase of optical damage resistance after CO_2 laser processing has been known since 1980 [34]. What is new here is local application to heal specific defects.

The typical time for relaxation of a surface disturbance with scale l is given by the estimate

$$\tau \sim \frac{\eta l}{\sigma} \quad (7.3)$$

The surface tension γ for glass is about 300 dyne/cm [35] and not very sensitive to temperature. In the range of 1600-2000°C, the viscosity η is given by the expression [36]

$$\eta = 1.05 * 10^9 e^{\frac{E}{T}} \text{ poise} \quad (7.4)$$

where E is an activation energy, E~6.44 eV. For a deep crack, we must use the crack depth for l . If we know the crack depth and the acceptable annealing time, we can determine from (7.3) and (7.4) the annealing temperature T.

Let us consider now crack mitigation by local heating. The time for crack healing is given by (7.3). During this time $d = V\tau$ of material will be ablated. The total amount of ablated material is given by the expression

$$d = \frac{\eta_0 l V_0}{\sigma} e^{\frac{E-U}{T}} = 1.75 * 10^6 e^{\frac{32944}{T}}$$

Here d and l are in microns, T in Kelvins. The amount of material ablated during the crack healing process as a function of surface temperature is presented in Fig.(11). One can see that for the temperature 2245K used above, ablation of more than 1.5 μm guarantees that the cracks in the subsurface layer will be annealed. Hence, in experiments [31] the laser-induced temperature must be high enough to heal the subsurface layer around the damage spot. Due to the nonlinearity of thermal conduction, the temperature distribution around the heated spot is pretty flat and the wide zone around is annealed of microcracks.

8. CONCLUSION

We demonstrated that the intrinsic damage threshold in silica for nanosecond pulses is well above the observed values. Damage is initiated at defects, mainly the surface imperfections produced by the polishing process. Improvement of the polishing process has been shown to increase damage threshold.

The model of small, nanoscale initiators is consistent with experimental data. The absorption of laser energy in an inclusion initiates a thermal explosion, formation of plasma fireball, and growth of the fireball up to a size comparable with laser light wavelength. The energy storage in the fireball is released as a microexplosion, forming a crater on the optics surface.

The damage crater is surrounded by mechanically and electronically modified material. The light radiation in this material results in damage spot growth with repeated shots. The damage growth has a fluence threshold. The size of the damage spot increases exponentially with number of shots, and growth takes place via generation of conical cracks on the spot periphery.

Growth of the damage spot can be mitigated by the removal of modified material. CO₂ laser annealing can efficiently mitigate local damage sites by removal of modified material and improvement of material structure around the damage spot.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. Authors acknowledge the fruitful discussions with A.K. Burnham, R.M. Brusasco, C.W.Carr, S.Demos, M.Fluss, L.A. Hackel, L.W.Hrubesh, M.R.Kozlowski W.A.Molander, M.A.Norton, B.M.Penetrante, P.J.Wegner,

REFERENCES

1. *Boulder Damage Symposium v.1-33.*
2. B. C. Stuart, M. D. Feit, S. Herman, A. M. Rubenchik, B. W. Shore, and M. D. Perry, "Nanosecond-to-femtosecond laser-induced breakdown in dielectrics", *Phys. Rev. B* 53, 1749 (1996).
3. D. Arnold, E. Cartier, D. DiMaria, "Acoustic-phonon runaway and impact ionization by hot electrons in silicon dioxide". *Phys. Rev. A* 45, 1477 (1992).
4. F. Rainer, F. DeMarco, M. Staggs, M. R. Kozlowski, L. J. Atherton, L. M. Sheehan, "A historical perspective on fifteen years of laser damage thresholds in LLNL" *SPIE Proc.*, Vol. 2114, pp 9-22, (1993).
5. Feit M.D., A.M. Rubenchik, M.R. Kozlowski, F. Genin, L. Sheehan, S. Schwartz, "Extrapolation of damage test data to predict performance of large-area NIF optics at 355 nm". *Proceedings XXX Annual Symposium on Optical Materials for High-Power Lasers*, Boulder, CO, Sept. 28-Oct. 1, 1998, SPIE-3578-48, pp. 226-231
6. M.D. Feit., A.M. Rubenchik, D. Faux, R. Riddle, D. Eder, B. Penetrante, D. Milam, F. Genin,
7. M. Kozlowski, "Modeling of Laser Damage Initiated by Surface Contamination", *Proceedings in Laser-Induced Damage in Optical Materials*, Boulder, Co, Oct -7-9, 1996 SPIE, pp. 2966-26 (1997).
7. L.M. Sheehan, M.R. Kozlowski, D.W. Camp, "Application of Total Reflection Microscopy for Laser Damage Studies on Fused Silica", *Proceedings in Laser-induced Damage in Optical Materials*, Boulder, CO, Oct 6-8, 1997 SPIE 3244, pp. 282-295 (1998).
8. L. Skuja, H. Hosono, M. Hirano, "Laser-induced color centers in silica," *Proceedings in Laser-Induced Damage in Optical Materials*, Boulder, CO. Oct. 16-18, 2000, SPIE-4347, pp. 155-168.
9. H.C. van der Hulst, "Light scattering by small particles", John Wiley and Sons, NY (1957).
10. Edward D. Palik, ed., "Handbook of Optical Constants in Solids", *Academic Press* (1985).
11. M.D. Feit, J.H. Campbell, D.R. Faux, F.Y. Genin, M.R. Kozlowski, A.M. Rubenchik, R.A. Riddle, A. Salleo, J.M. Yoshiyama, "Modeling of laser-induced surface cracks in silica at 355 nm", *Proceedings in Laser-induced Damage in Optical Materials*, Boulder, CO, Oct 6-8, 1997 SPIE 3244, pp. 350-355 (1998).
12. M.R. Lange, J.K. McIver, A.H. Guenther, T.W. Walker, "Pulsed laser induced damage of an U.S. Spec. Publ. 669, pp. 380-6, (1984).
13. M.D. Feit., A.M. Rubenchik, M. Runkel, "Analysis of bulk DKDP damage distribution, obscuration and pulse length dependence", *Proceedings XXXII Annual Symposium on Optical Materials for High-Power Lasers*, Boulder, Co, Oct. 16-18, 2000, SPIE-4347, pp. 383-388 (2001).
14. N. Blombergen, "Laser induced electric breakdown in solids", *IEEE J. of Quantum Electr.*, 10, 375, (1974).
15. F. Genin, A. Salleo, T. Pistor, L. Chase, "Role of light intensification by cracks in optical breakdown on surfaces". *JOSA A* 18, 2607-2616, (2001).
16. A. V. Hamza, W. J. Siekhaus, A. M. Rubenchik, M. Feit, L.L. Chase, S. Demos, M. Savina, M. J. Pellin, M. J. Fluss, M. C. Nostrand, M. Runkel, B. W. Choi, M. Staggs, and I.D. Hutcheon, "Engineered defects for investigation of laser-induced damage of fused silica at 355nm", *Proceedings in Laser-Induced Damage in Optical Materials*, Boulder, CO., Nov. 1-2, 2001, SPIE, (2002).
17. J. Menapace, B. Penetrante, D. Golini, A. Slomba, P. Miller, T. Parham, M. Nichols, J. Peterson, "Combined advanced finishing and UV laser conditioning for producing UV damage resistant fused silica optics", *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Nov. 1-2, 2001, SPIE, (2002).
18. C.W. Carr, H.B. Radousky, M. Staggs, A.M. Rubenchik, S.G. Demos, "Time-resolved spectroscopic investigation of emission observed during damage in the bulk of KDP crystals", *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Nov. 1-2, 2001, SPIE, (2002).
19. P. Grua, H. Bercegol, "Dynamics of electrons in metallic nanoinclusions interacting with an intense laser beam". *Proceedings XXXII Annual Symposium on Optical Materials for High-Power Lasers, Boulder, Co, Oct. 16-18, 2000, SPIE-4347*, pp. 579-587
20. H. Melosh. "Impact ejection, spallation and the origin of meteorites". *Icarus* 59, 234-260, (1984)
21. M.D. Nordyke "An analysis of cratering data from desert alluvium", *J. Geophys. Res.* 67, 1967-1974, (1962)
22. M.D. Feit., L.W. Hrubesh, A.M. Rubenchik and J. Wong, "Scaling relations for laser damage initiation craters", *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Oct. 16-18, 2000, SPIE-4347, pp. 316-323, (2001).
23. N. Bourne, J. Millet, J.E. Field "On the strength of shocked glasses," *Proc. R. Soc. A.* 455, 1275-82, (1999).
24. F. Bonneau, P. Combis, J. Vierne, G. Daval, "Simulations of laser damage of SiO₂ induced by a spherical inclusion", *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Oct. 16-18, 2000, SPIE-4347, pp. 308-315, (2001).

25. S.Papernov, A.Schmid, R.Krishnan,L.Tsybeskov, "Using Colloidal Gold nanoparticles for studies of laser interaction with defects in thin films.", *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Oct.16-18, 2000, SPIE-4347, pp.146-154, (2001).
26. A.K. Burnham, M.Runkel, S.Demos, M.R. Kozlowski, P. Wegner, "Effect of vacuum on the occurrence of UV-induced surface photoluminescence, transmission loss and catastrophic surface damage", *Photonics for Space Environments VII*, Proc. SPIE, v.4134 pp.243-252, (2000).
27. H.Philip, "Optical properties of non-crystalline Si, SiO, SiOx and SiO₂. *J.Phys.Chem.Solids* 32.1935-45, (1971).
28. J.Wong, D.Haupt, J.Kinney, J.Ferriere, I.Hutcheon, S.Demos, M.Kozlowski, "Nature of damage in fused silica induced by high-fluence 3 ω 355-nm laser pulses, a multiscale morphology microstructure and defect chemistry study", *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Oct.16-18, 2000, SPIE-4347, pp. 466, (2001).
29. A. Kubota, L. Davila, M.J. Caturla, J. S. Stolken, B. Sadigh, A. Quong, A. Rubenchik and M. D. Feit, "Structural modifications in fused silica due to laser damage induced shock compression," *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Nov. 1-2, 2001, (2002).
30. M.Norton, L.Hrubesh, Z.Wu, E.Donohue, M.D. Feit, M.Kozlowski, D.Milam, K.Neeb, W.Molander, A.M. Rubenchik, W.Sell, P.Wegner, "Growth of laser initiated damage in fused silica at 351 nm", *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Oct.16-18, 2000, SPIE-4347, pp. 468, (2001).
31. L.W.Hrubesh, M.A.Norton, W.A.Molander, E.E.Donohue, S.M.Maricle, B.M.Penetrante, R.M.Brusasco, W.Grundler, J.A.Butler, J.W.Carr, R.M.Hill, L.J.Summers, M.D.Feit, A.Rubenchik, M.H.Key, P.J.Wegner, A.K.Burnham, L.A. Hackel, M.R.Kozlowski. "Methods for mitigating surface damage growth on NIF final optics." *Proceedings in Laser-Induced Damage on Optical Materials*, Boulder, CO., Nov. 1-2, 2001, (2002).
32. S.I. Anisimov, V.A.Khokhlov "Instabilities in Laser-matter interaction", CRC Press Boca Raton, (1999).
33. H.Schoize, *Glass*, Springer- Verlag, (1991).
34. Temple, P.A.; Lowdermilk, W.H.; Milam, D.; "Carbon dioxide laser polishing of fused silica surfaces for increased laser-damage resistance at 1064 nm", *Appl. Opt.* 21, 3249-55 (1982).
35. "The Handbook of Glass Manufacture", 3rd ed.. Vol. 2, p.930 Ashlee Publishing Co. (N.Y. 1984).
36. D.Hewak, Ed., "Properties, processing and applications of glass and rare earth-doped glasses for optical fibres", London, UK: INSPEC, (1998).