Laser damage probability studies of fused silica modified by MeV ion implantation

T.E. Felter *, L. Hrubesh, Alison Kubota, Lilian Davila, Maria Caturla

Lawrence Livermore National Laboratory, Livermore, CA 94551-0808, USA

Abstract

Energetic ions in the MeV regime have pronounced effects on the stress-state and geometry of fused silica. In particular, Polman and co-workers have shown that 4 MeV xenon ions cause substantial changes in thin films and microspheres of fused silica. For example, 2 μm wide trenches in thin films can be partially closed and microspheres substantially distorted. In our study, we investigate implantation into bulk silica and the subsequent response to high intensity ultra violet light. Specifically, we compare the damage threshold of fused silica to intense ultra violet light at 355 nm before and after room temperature ion bombardment and find little change despite clear alteration of the stress-state in the glass. We have also performed molecular dynamics simulations in order to understand the underlying effects that lead to obscuration of optics under laser and ion irradiation.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Laser damage threshold; Fused silica; Ion implantation; MeV; Xenon; High intensity ultra violet light; Molecular dynamics; Modification of materials by ion beams; Radiation effects; Initial compaction or densification; Plastic deformation; Feuston and Garofalini potential

1. Introduction

A major concern for the designers of high photon flux optics is the possible failure of optical components that are subjected to high intensity laser light. Once damage sites have been initiated, continuing pulses of laser light could lead to increased damage. Density changes and structural imperfections such as micro-fissures may be associated with damage propagation. In this study, we investigate whether ion beams, which have been shown to be useful in changing geometry and stress-state of silica [1–5], can be used to help understand or alter the effects of high intensity laser light.

Fused silica is selected for high-flux optics because its high bulk purity leads to low absorption and hence the ability to transmit a large photon flux without damaging the bulk. At sufficiently high energy density from a pulsed coherent light source, damage may initiate at the exit surface. Once damage in the surface and near surface regions has been initiated, continued damage may occur with subsequent pulses. Methods used to create compressional layers and therefore strengthen conventional glass, cannot be directly applied to fused silica. These include physical methods of surface melting and rapid quenching and chemical methods such as ionic exchange reactions with molten...
potassium nitrate. Silica, however, sublimes rapidly near the melt temperature and contains no ions to exchange, thwarting these physical and chemical methods, respectively. Ion beam modification of silica surfaces, offers an opportunity for altering the compression/tension stress-state for studying the laser damage mechanism.

Improving the toughness of silica glass by the formation of a compressive surface would have widespread utility far beyond specialized high power optical applications simply by increasing the mechanical strength of this important technological material. High optical power applications include a large number of military and commercial technologies, for example: airborne, satellite and ground based laser weapons [6] and large lasers for manufacturing (cutting, welding, ablating, finishing, etc.). In addition, modification of optical materials by ion beams could lead to advances in imaging, opto-electronics, fiber optics (including sensors based on fiber optics) and micro-machining. Compaction and related effects in fused silica caused by ion beams can elucidate similar processes caused by uv radiation and currently of great worry to the developers of a viable 193 nm lithography technology [7]. Moreover, there is a continuing scientific need to study the modification of materials by ion beams [8].

Polman and co-workers have studied the effects of energetic heavy ions on the stress-state of fused silica [2–5] using 4 MV xenon ions. To continuously monitor the stress of the silica, they employed an in situ bending lever of silicon coated with approximately 2 μm of silica [3,5]. The incident xenon traversed the silica layer and stopped in the underlying silicon. Even for their largest doses, $1 \times 10^{14}$ Xe/cm², the total atomic volume of the xenon implanted into the silicon lever is small and only a small correction to their large measured stress in the silica was required. They identified three regimes of interest in the changes induced in the silica coating. (1) Initial compaction or densification. (Density changes as an exponential decay from the virgin material to the saturated density at a characteristic fluence of $1 \times 10^{13}$ Xe/cm².) (2) Newtonian viscous flow. (3) Anisotropic plastic deformation. Although process 3 never saturates, process 2 counters the effect and steady-state is reached at $1 \times 10^{14}$ Xe/cm². At these doses, compressional forces can be achieved.

For a confined system, such as the bending lever, the steady-state balance of Newtonian viscous flow with the anisotropic plastic deformation places the surface in a compressive state of greater than 60 MPa for ion energies larger than 4.0 MeV. For unconfined systems – e.g. approximately 2 μm thick SiO₂ on silicon with frequent 2 μm wide trenches, the non-saturating anisotropic plastic deformation causes lateral flow leading toward closure of the trench [3]. Recent work with silica spheres shows that pronounced shape changes can be induced by this effect [4].

2. Experimental results

In order to achieve these ion doses with our single ended 4MeV Pellatron at reasonably short times we did not use our rastered beam line. Instead, a LabView™ based software, written for the Windows NT environment, was developed to scan the sample stage stepper motors of our ion beam analysis line. The beam slits were set at 3 mm × 3 mm and the smallest uniform area was 5 mm × 5 mm. The program permits x and y scanning of the stage in a raster pattern. The x and y travel limits, step sizes, and velocities are independently controlled. In our actual ion irradiation experiments, we chose areas of a few square millimeters to several square centimeters – depending on the experiment. This capability permits doses of three orders of magnitude greater than we are able to achieve with our rastered beam line. Samples were 50 mm in diameter, 10 mm thick and firmly clamped to a 200 mm diameter aluminum plate 10 mm thick. Table 1 lists the species, energy and ion dose for the work performed. Those results showed that high ion fluences caused optical damage of the glass. The damage was found to be in the form of minute cracks in the surface, or "crazing".

For our first experiments, we ion irradiated fused silica samples at room temperature that had previously been exposed to intense laser light at 355 nm and therefore contained laser damage craters. The 4 MV ion irradiated samples were
inspected visually and by optical microscopy. Optical micrographs before and after showed no indication of reflow or closure. Although more sensitive measurements with scanning electron microscopy may have indicated minor changes – another effect was seen which made further study unwarranted: craze-type cracks initiated in the implant area. Samples that developed these cracks are described in the comments section of Table 1 with “crazed” and laser damage curves were not obtained for them.

We also initiated low ion dose studies to investigate the effect of energetic ion beams on damage probability. Generally, half of the 50 mm diameter silica disk was irradiated with ions. The unirradiated half circle of the sample served as a control specimen. Unfortunately, a stage capable of heating or cooling the large specimens was not available for this preliminary study. Xenon ions were employed in order to correlate with Polman’s studies. Oxygen ions were employed since they are a component of the substrate. The large area low dose samples were then exposed to 355 nm light.

The laser exposure consists of a series of pulses, starting at low energy density and ramping upward to higher energy density. In situ diagnostics detect when damage occurs and this signal is used to immediately halt the laser pulses. The diagnostics are based on diffuse scattering from a low power cw (continuous wave) laser or from light emission from the damage plume. The energy density at which damage occurred is recorded and a new part of the sample is positioned for the next series of pulses of the energy density ramp procedure. This is done for a number of new sites, generally eight. The energy density at which damage occurred is plotted to create a “damage probability curve”, see Fig. 1, which is generally described as an S-shaped curve.

Figs. 2 and 3 show damage initiation curves for xenon and oxygen ions, respectively, at relatively low ion doses. The squares represent the damage probability curve for the untreated half circle of the sample while the triangles are the results of the ion implanted region. Within the coarse statistics available in this study, the ion-treated and non-treated surfaces behave identically. However, in the implanted region, the size and extent of the damage was more severe. We frequently found cracks emanating radially from the damage sites for distances on the order of millimeters.

For SiO₂ grown on silicon substrates, as in Polman’s work, the SiO₂ is initially in a compressed state. This comes about by the high temperature oxidation process used to form the silica film on the underlying silicon substrate. Upon cooling – the differential contraction places the SiO₂ in compression. In other words, the silicon contracts more than the SiO₂. The via closing effect is due to the ion induced flow, allowing the initial compressed state to relax, without cracks forming.

In our case, there is no substrate to form initial compression at the near surface. Ion irradiation

Table 1
Summary of ion irradiation conditions

<table>
<thead>
<tr>
<th>Area irradiated</th>
<th>Ion@energy</th>
<th>Dose</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mm patches</td>
<td>Xe⁺@3.4 MeV</td>
<td>5e14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5e15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5e16</td>
<td></td>
</tr>
<tr>
<td>5 mm patches</td>
<td>Xe⁺⁺@13.6 MeV</td>
<td>3e12</td>
<td>S data 8 pts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1e13</td>
<td>S data 8 pts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3e13</td>
<td>Surface crazed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6e13</td>
<td>Surface crazed</td>
</tr>
<tr>
<td>1/2 inch strip</td>
<td>Xe⁺⁺ @13.6 MeV</td>
<td>1e12</td>
<td>S data 19 pts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3e12</td>
<td>Surface crazed</td>
</tr>
<tr>
<td>1/2 inch strip</td>
<td>O⁺@3.4 MeV</td>
<td>3.6e12</td>
<td>S data 8 pts</td>
</tr>
<tr>
<td>1/2 inch strip</td>
<td>O⁺@3.4 MeV</td>
<td>1.4e13</td>
<td>Surface crazed</td>
</tr>
</tbody>
</table>
causes the silica to densify which immediately places the surface in tension. For low ion doses, tensile cracks can be initiated by intense laser light. For larger doses, the cracks self initiate. This stress promotes the propagation of damage features – namely, surface cracks. Thus, the ions have had a significant effect on the stress-state and structural properties of the surface.

The fact that the damage probability curves are independent of significant changes in the stress-state of the glass induced by the ions suggests that the initiation sites are caused by features not affected by substantial changes to the structure of the glass. Small particles or inclusions of contaminants have recently been proposed as the damage initiators [9]. Our results are in accord with such a mechanism since the ion irradiation would not remove such contaminants.

As far as damage probability is concerned, Figs. 2 and 3 are in the limit of low ion dose. That is, the dose is sufficiently small as to cause no change in the measured property of damage probability. It is clear, however, that changes to the glass have occurred since investigation of the damage site indicates damage propagates further from the site. At higher ion doses, similar long cracks are seen even without exposure to the laser beam. We believe these features, both low dose laser initiated, and higher dose self-initiation, are due to ion beam induced compaction. The doses occur in the steep
downward region in Brongersma’s work, Fig. 1 [2]. This self-damage at low dose prevents useful measurement at high dose wherein a compressional state is achieved. It is important to understand why this occurs in the case of bulk SiO$_2$ – but not the cantilever nor the micro spheres in Polman’s work [2–5].

In the case of the micro spheres, the system is unconfined [4]. Rather than entering a tensile state, the sphere simply distorts. At higher ion doses, where anisotropic viscous flow occurs, the sphere flattens, or thins, in the direction of the ion beam and expands in the two directions perpendicular to it. In the case of the SiO$_2$/Si cantilever beam, the SiO$_2$ is thermally grown on the silicon substrate. Upon cooling – the silicon contracts more than the SiO$_2$ creating a compressional force. Ion irradiation, reduces the compressional forces and even creates a tensile stress – but of lower magnitude than required to create cracks. In other words – the silicon substrate supports the silica in a beneficial fashion. Thus, with a silicon substrate, continued ion beam exposure is possible without forming cracks and a compressive state can be achieved at the larger doses. It is important to note that other ion implant conditions, such as ion species and energy and the substrate temperature will have a strong effect on the nature of the stress-state achieved by ion implantation. In particular, it should be possible with suitable conditions to achieve a compressional stress without forming surface cracks.

3. Molecular dynamics

We have also performed molecular dynamics simulations in order to understand the underlying effects that lead to obscuration of the optics both under laser and ion irradiation. Damage sites produced by high-flux laser irradiation show a densified surface layer at the bottom of the craters surrounded by fractured material [10]. Our simulations [11] have shown that this densified layer can be produced as a result of a shock wave, supporting the hypothesis of a localized absorber in the optic that induces a plasma [9]. These simulations also reveal a change in the structure of this densified layer. Although the amorphous structure and coordination is preserved, this densified structure presents a different ring distribution with respect to the pristine silica glass. An increased number of 3 and 4 member rings are present in this modified material, in agreement with Raman spectroscopy measurements [12]. The number of 6-member rings is reduced and an increase in larger rings is also observed, as shown in Fig. 4. This figure presents the ring distribution before and after applying a shock wave generated by a piston at a velocity of 2.5 km/s. The shock wave results in a modified material with density 20% higher than the initial silica glass, in agreement with experiments [10].

These changes in structure raise questions regarding the absorption of this new material at the wavelength of interest. An increase in absorption of this densified layer would explain the rapid increase in damage after repeated laser pulses. In order to address this issue, we have performed first principles calculations to obtain the absorption as a function of wavelength for fused silica, and fused silica with an increased number of 3-member rings, as shown in Fig. 5. These calculations we performed using the commercial package CASTEP [13] with 48 atoms supercells. The initial amorphous structure was generated using the same empirical potential as in the shock calculations mentioned above, the Feuston and Garofalini

![Fig. 4. Ring size distribution for fused silica before and after a shock wave of velocity 2.5 km/s, resulting in a 20% increase in density.](image-url)
The first principle calculations were done using an ultra-soft pseudopotential. Due to the presence of the 3-member ring in the modified structure the band gap narrows, shifting the absorption towards longer wavelengths, as shown in Fig. 5. This effect is an indication of an increased absorption of this modified material at the wavelengths of interest. However, other features, like cracks under the compressive layer, could also contribute to the increased absorption at the damaged sites.

Ion irradiation can also induce densification, as mentioned above. Neutron irradiation studies have shown a 2% increase density after irradiation [15]. However, irradiation also generates electronic defects that act as absorbers, or ‘color centers’. Some of these defects are the so-called E’ center and the non-bridging oxygen hole centers [16]. A saturation of the total number of defects produced with dose has been observed in ion irradiation studies [17]. We have performed molecular dynamics simulations to study the effects of energetic recoils in the fused silica glass. Fig. 6 shows the track of an atom with 5 keV energy as it travels through the silica glass. Blue dots indicate the position of 3-fold coordinated silicon atoms, that is, oxygen vacancies. These oxygen vacancies are the pre-cursors for E’ centers. We have studied the saturation of the number of steady-state defects with dose. Simulations of successive cascade overlap of 1 keV recoils show that after approximately 5 successive impacts the number of steady-state defects remains constant, as presented in Fig. 7.

Topological changes are also observed in simulations of ion irradiation. In particular, we observe an increase in the number of 3 and 4 member rings, indicative of densification, as in our previous calculations of shock propagation. These topological changes also saturate with dose, although at higher ion doses than the defect saturation. From our simulations with 1 keV recoils, the changes in 3 and 4 member rings saturate after 9 recoils. This saturation effect of densification has also been observed.
experimentally [18]. Fig. 8 shows the spatial distribution of 2, 3, 4, 10 and larger rings in our molecular dynamics simulations. The smaller 2-, 3- and 4-membered rings are shown as dark loops while the larger rings are shown with bright loops. The indicated regions demarcating the cascade region in Fig. 8 clearly show the increase in the smaller 3- and 4-membered rings. The localized densification of the structure will create tension in a constrained system, which can result in the formation of cracks as observed in the experiments presented in this paper.

4. Conclusion

Heavy ion bombardment in the MeV regime has been used to modify surfaces of silica glass at room temperature. The implantation significantly changes the stress-state as verified by self initiated surface cracks at moderate doses and laser induced cracks at lower doses. The results for our particular implant conditions are consistent with a surface placed in tension. Despite the implied change in structure by the ion implantation, laser damage probability was not affected. This suggests that the structure of the glass itself is not the dominant contributor to the initial laser damage to the glass. Such a finding is consistent with an extrinsic defect serving to initiate the damage. Such defects include small particulate contaminants as suggested in other recent studies of laser damage. With other
implant conditions it may be possible to heal defects, place the surface in compression, make the surface region more bulk-like, and improve optical characteristics at high photon flux.

Molecular dynamics simulations show that irradiation generates point defects that can act as color centers. At the same time, irradiation also induces topological changes associated with densification. These changes are localized along the track of the energetic ions, and saturate at doses higher than the saturation of the electronic defects.

Acknowledgements

The authors appreciate thoughtful suggestions and conversations with T. Diaz de la Rubia, Teun van Dillen, M. Fluss and R.G. Musket. The technical assistance of Stephen Maricle is gratefully acknowledged. This work was performed under the auspices of the US Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract no. W-7405-Eng-48.

References