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Cathodoluminescence Microanalysis of the Distribution of Defects Induced in Fused Silica by UV Laser Pulses and After Damage Mitigation Treatment with a CO_2 Laser.

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Abstract

Point defects are induced in high quality optical-grade fused silica by high fluence (>30 J/cm^2) 355nm laser pulses. The microscopic depth distribution of laser irradiation induced defects has been nondestructively determined using Cathodoluminescence (CL) microanalysis. CL emissions have been observed at 1.9eV, 2.2eV, 2.7eV and 4.4eV. In addition following CO_2 laser treatment for damage mitigation an emission at 3.2eV is also observed. The CL emissions have been identified with the NBOHC (non-bridging oxygen hole center), the STE (self-trapped exciton), an ODC (oxygen-deficient center) and an aluminum impurity centre. The spatially resolved CL data is consistent with damage initiation at the exit surface. The concentration of 355 nm laser induced defects is greatest at the surface and monotonically decays to pre-irradiation levels at ~10 μm depth below the surface. With CO_2 processing to mitigate damage, the defect concentration and spatial distribution is reduced to a maximum depth of ~6μm. CL microanalysis provides a sensitive and nondestructive method of assessing the magnitude and submicron distribution of irradiation induced damage in technologically important materials.

Introduction

Recent industrial interest in far ultraviolet (UV) lithography for microelectronics and telecommunication,[1] has excited considerable scientific and technological interest in UV laser-induced damage processes induced in materials used for transparent optics[2,3] in particular silicon dioxide (SiO_2) (see Hosono et al[4] and Kajihara et al[5] and references therein). Multi-disciplinary methods are being applied in an effort to understand the nature of laser-material interaction leading to damage initiation and development. In addition technically viable solutions are being sought to prolong the lifetime of optical components by reducing susceptibilities to laser-induced catastrophic breakdown. Because of its excellent optical transparency and uniformity in the UV region, high quality fused silica (SiO_2) is the material of choice for use in high-average and high-peak power laser systems.[6-8]

Obscuration loss and near-field intensity modulation resulting from laser-induced damage on the optical surfaces largely determines the operational lifetime of SiO_2 components. The obscuration arises from two processes: initiation of damage at an absorbing site at or near the exit surface, and damage growth upon subsequent irradiation. While defects on polished silica optics due to contamination and subsurface defects induced by polishing processes have been minimized,[9] the currently attainable surface defect densities can still result in an unacceptable number of damage initiation sites on optics used in high power UV laser systems. Techniques for inhibiting the growth of UV laser-induced surface damage on fused silica are being developed and investigated.[10] The technique that has been found to be most consistent and effective at stopping the growth of the laser damage in the fused silica optics is the CO_2 laser processing technique.[10,11]

The pre-initiated damage sites are exposed to single pulses of a CO_2 laser to locally treat the laser damage ensuring it does not propagate further. Systematic complementary evaluations of UV laser-induced damage sites in fused silica following damage initiation and after mitigation with CO_2 laser processing determining the material morphology[12] structural defects[13] and defect distribution will aid identification of the damage initiators and help to elucidate the mechanism associated with the damage initiation, damage growth and mitigation processes. This will enable the development of a knowledge-based methodology to mitigate or preclude laser induced damage.

This paper reports the non-destructive cathodoluminescence (CL) micro-analysis of the spatial distribution of point defects induced in fused silica by high fluence 3ω, 355nm laser pulses following damage initiation and after damage mitigation using a CO_2 laser treatment process. The corresponding laser induced morphology and microstructure in SiO_2 are reported elsewhere.[12,13] Cathodoluminescence (CL) is the non-incandescent emission from a material irradiated with electrons. CL microanalysis (spectroscopy and microscopy) in a scanning electron microscope (SEM) enables high sensitivity detection of diamagnetic and paramagnetic defects. Local variations in the bulk and surface defect structure can be nondestructively characterized with high spatial (lateral and depth) resolution by adjusting electron beam parameters to select the specimen micro-volume of interest.[14] CL complements the defect structure information available from electron spin resonance (ESR) and optical spectroscopic techniques. To our knowledge, this is the first non-destructive determination of the microscopic depth distribution of defects in fused silica irradiated with high fluence laser pulses. These results complement and are consistent with published data on the irradiation response of fused silica and give insight

into the fundamental processes associated with UV irradiation induced defect generation in this technologically important material.

Experiment

The fused silica substrates were 50mm diameter x 10mm thick, and optically polished on both surfaces. The fused silica which is characterized by a low thermal expansion co-efficient and excellent UV optical properties, is manufactured by flame hydrolysis and contains 800-1000ppm by weight of OH (Corning 7940[15]). For CL experiments, 10 mm cubes were cut prior to laser irradiation. During cutting the optical surfaces were protected with a solvent-removable paint. Laser damage sites were created in ambient conditions using a 3ω, 355 nm beam from a frequency tripled Spectra Physics GCR Nd-YAG laser with pulse length (full width half maximum) of 7.5ns and laser repetition rate of 10.[16] The beam profile was near-Gaussian with a $1/e^2$ diameter of ~0.9mm at the sample plane. Damage sites were produced exclusively on the laser exit surface[17] using single or multiple pulses with fluences ranging from 30-45 Jcm^{-2}. Damage sites were separated by several mm.

The CL experiments were performed in a SEM equipped with a *Gatan/ Oxford Instruments* MonoCL2 cathodoluminescence imaging and spectral analysis system. The CL was excited using a continuous stationary electron beam at normal incidence, and measured using a retractable diamond machined paraboloidal mirror collector. CL spectra were collected by photon counting using a *Hamamatsu R943-02* Peltier cooled high sensitivity photomultiplier using a 1200 line/ mm grating, blazed at 500nm. In energy space the CL emission bands generally have a Gaussian profile,[14] and this is particularly

the case for defects involving the silicon dioxide tetrahedral structure which typically have Huang Rhys factors of ~10 [18] due to relatively strong defect-lattice coupling. CL spectra which are collected as a linear function of wavelength λ(nm), were therefore converted to energy E(eV), and corrected for total instrument response prior to peak fitting/ componentization.[19-21] The total instrument response has been determined experimentally from NIST traceable standard lamps. The response function is a non-linear and smoothly varying function between ~250-900nm. The instrument response is ~10% of maximum at ~275nm, monotonically increases to a maximum at ~500nm then decreases to ~10% of maximum at ~850nm and to a minimum at ~900nm. The estimated maximum uncertainty in the CL emission intensities is ~5% where the system response is poor, and <0.5% (at ~2eV) where the system response is optimized. For spectra with broad emissions, such as is typical for silicon dioxide, it is essential to correct for instrument response to avoid errors in the band profiles and energy positions. Discrepancies in emission energy positions, peak shapes and relative intensities in the SiO_2 luminescence literature may be at least partially attributed to the lack of instrument response corrections in some reports.

Results and Discussion

Damage initiation

There are significant differences between CL spectra and spatially (lateral and depth) resolved images from the laser damaged and undamaged fused silica surfaces. The intensity of the CL emission is low from this high quality pure fused silica. Fig. 1 shows

typical experimental CL spectra collected from (a) unirradiated silica and (b-d) 3ω, 355nm laser irradiated silica. The CL emission was excited with a normal incidence electron beam from ~170^2 μm^2 regions (ensuring all damage features were included, and equivalent specimen volumes were sampled). The spectra in Fig. 1 were excited with a 25keV, 1.5nA electron beam. The number of spectra included in each data set, the beam current, beam power density and spectral collection times were minimized to reduce electron irradiation induced effects, as silicon dioxide polymorphs are susceptible to electron beam induced radiation.[22]

CL emissions are observed at 1.9 eV and 2.7 eV from the undamaged specimens. The CL spectra collected from different regions of the undamaged specimens are the same indicating uniform distributions of pre-existing defects prior to laser irradiation, as expected from homogeneous high purity fused silica. As has been reported previously[13], following laser irradiation the intensities of the 1.9 eV and 2.7 eV emissions increase. In addition, low intensity emissions at 2.3 eV, 4.4 eV and 0.97 eV (not shown) may also be observed (e.g. see Fig. 1(d)).[13] An increase in laser power and/or number of laser pulses enhances the CL emission indicating increases in the concentration of associated defects. The CL emissions can be identified with a variety of known fundamental point defects. The observed defects resulting from the high fluence laser irradiation are consistent with those resulting from other energetic irradiations (e.g. electron,[22,23] ion,[24] x-ray,[25] γ ray,[26] etc).

In defect free silica, each silicon atom is surrounded by four tetrahedrally co-coordinated oxygen atoms and adjacent silicon atoms are bridge bonded through a single oxygen atom. The local defect free tetrahedral SiO_2 bonding structure can be simply denoted as $O_3{\equiv}Si\text{-}O\text{-}Si{\equiv}O_3$, where the dashes represent silicon-oxygen bonds. In crystalline SiO_2 the bond lengths and the Si-O-Si bond angles connecting the silicon dioxide tetrahedra are well defined.[27] There is a broader range of slightly different atom sites in the random amorphous structure of fused SiO_2.[28] Although the basic tetrahedral configuration is maintained in amorphous SiO_2, the local lattice structure is less dense, more easily deformed and there is more local disorder due to slightly different bond lengths and a range of bond angles.[27]

The 1.9eV emission is associated with the non-bridging oxygen hole center (NBOHC) and attributed to the recombination of electrons in the highly localized non-bridging oxygen band-gap state, with holes in the valence band edge[29] and is denoted $O_3{\equiv}Si{-}O\bullet$ where (•) represents an unpaired electron.

Irradiation of amorphous SiO_2 produces luminescence at energies between 2.2-2.6eV, which has been attributed to the radiative recombination of the STE (see Stevens-Kalceff[20] and references therein). The low intensity 2.3 eV emission observed following laser irradiation is possibly associated with the self trapped exciton (STE) which is a correlated electron-hole pair localized in a self-induced lattice distortion. The radiative relaxation of the STE restores the local tetrahedral structure, $O_3{\equiv}Si\text{-}O\text{-}Si{\equiv}O_3$. It is noted that luminescent emissions (such as the STE) that are difficult to observe by photo-excitation may be more readily observed using CL techniques.[30] Localized thermal

annealing of the molten core region associated with the laser induced thermal explosion[12] results in the reduction in concentration of competitive non-radiative defect centers, which may thereby enhance the STE emission within the molten core region.

In addition, the observation of STE emission in the CL experimental spectra is consistent with the complementary Electron Spin Resonance (ESR) spectroscopy data showing significant concentrations of high fluence 3ω, 355nm laser irradiation induced E' type oxygen deficient centers.[13] The general form of the E′ center is denoted $O_3{\equiv}Si{\bullet}$ which represents an unpaired electron (•) in a dangling tetrahedral sp^3 orbital of a single silicon atom (Si) bonded to three oxygen atoms ($O_3{\equiv}$) in the SiO_2 structure (i.e. threefold coordinated silicon). E' centers are not associated with any known luminescence within the detection range of these experiments. However excitation of these E centers and other defect centers by the electron beam during CL measurements may allow localized complementary defect pairs to be annealed via radiative relaxation processes including STE emission. In fused silica examples of complementary defect pairs include oxygen deficient (e.g. E′ centers, two-fold coordinated silicon centers or oxygen vacancies) and oxygen excess centers (e.g. oxygen interstitials, peroxy radicals or NBOHCs).[28,31] Radiative decay of the STE from the electron beam induced annealing of laser irradiation induced E' centers with NBOHCs for example, results in the restoration of the defect free SiO_2 tetrahedral structure. This electron beam induced annealing may be energetically preferred depending on dynamic factors such as local strain in the damage craters. An example of a possible electron beam annealing process is $O_3{\equiv}Si{\bullet}$ *(E')* + $\bullet O\text{-}Si{\equiv}O_3$ *(NBOHC)*$\rightarrow$*e beam excitation*$\rightarrow$ $O_3{\equiv}Si\text{-}O\text{-}Si{\equiv}O_3$ *(defect free SiO_2)* + 2.3eV emission

(*CL*). Thus the observation of the 2.3 eV CL emission may indirectly confirm the presence of the laser irradiation induced E' centers, consistent with ESR observations.

The 2.7eV and (very low intensity) 4.4eV emissions are attributed to transitions involving an oxygen deficient defect (ODC). The most commonly proposed models for the oxygen deficient centers include the ODC(I) and ODC(II) centers. In the ODC(I) or relaxed neutral oxygen vacancy (≡Si–Si≡) the adjacent silicon atoms relax towards the vacancy site and form a covalent bond.[32] Two models are proposed for the ODC(II) including the un-relaxed neutral oxygen vacancy (≡Si…Si≡), where the original silicon atom positions are maintained,[33] and the two-fold coordinated silicon defect (=Si:).[26] CL data cannot uniquely distinguish between the models and the data is consistent with either or all of these defects. The infrared 0.97eV emission[13] (not shown in Fig. 1) has been identified as the singlet oxygen transition associated with interstitial neutral molecular oxygen dissolved in the relatively open vitreous silica structure.[22,34]

CL microanalysis enables the microscopic spatial distribution of individual defects to be determined using monochromatic (i.e. wavelength/energy selective) imaging. The radial spatial distribution of defects induced by the 3ω, 355nm high fluence laser damaged fused silica has been reported previously.[13] Comparison of the secondary electron image (topography) and CL image from laser damaged fused silica damaged by a pulse of 3ω, 355nm laser photons at 45 Jcm^{-2} is shown in Fig. 2(a, b, c and d). It can be seen that the CL emission is spatially correlated with the molten core regions produced by thermal explosion and the near concentric regions of fractured material resulting from the laser generated shock wave. Fig.2(c and d) shows the CL images of a damage crater

excited with a 15keV electron beam which penetrate to a maximum depth of ~2.15 μm and ~5 μm respectively, in fused silica. Thus the CL is generated closer to the surface at lower beam energy and the 15 keV image shows a stronger correlation with surface features than the 25 keV image. In particular, comparison of the secondary electron image (topography) and CL image in Fig. 2(e and f) indicates the molten nodules and micro-fibers resulting from the thermal explosion[35] are composed of strained oxygen deficient silica. Thus CL data is consistent with altered glass topology resulting from enhanced local strain in the vicinity of the laser damaged regions associated with mass loss (desorption and ejection) and/or densification (observed high concentration of oxygen deficient centers) due to laser generated shock waves and thermal explosion.[12]

Depth resolved information on defect distribution in a material can also be determined non-destructively from CL microanalysis. This is achieved by varying the electron beam energy and hence the depth at which the CL emission is generated, while keeping the beam power constant.[36] Visible CL spectra have been collected for a range of energies between 7-40 keV, from both undamaged and laser damaged fused silica (See Figure 3(a)). The spectra are then fitted with Gaussian components using a non-linear least squared fitting algorithm (see typical example shown in Fig 3(b)). The experimental integrated CL intensities for each emission component are plotted as a function of electron beam energy (see point plots in Fig. 4(a), (b) and (c)). Fig 4(a) has been collected from a typical series of spectra from unirradiated (as received) fused silica. Fig 4(b) and (c) have been collected from high fluence 3ω 355nm laser damaged fused silica following one and two 30 Jcm^{-2} pulses respectively.

CL intensity is proportional to the electron-hole pair generation by the electron beam which is dependent on the energy transfer processes within the specimen. The CL intensity, I_{CL} may be expressed as the integral over the energy transfer function, dE/dz and the depth distribution of CL centers, n(z), where α is a constant and R is the maximum electron range depending on E_0 [36]

$$I_{CL} = a \int_0^R \frac{dE}{dz}(E_0) \; n(z)\, dz \qquad \text{Equation 1}$$

The energy transfer function, dE/dz for SiO_2 has been experimentally determined and verified[36] and is plotted (for beam energies relevant to these experiments) in Fig. 5. The depth distribution of defects, n(z) can then be determined from the experimental CL intensities. As the volume from which the CL signal is collected is not constant, an iterative approach assuming a range of functions for n(z) has been used to calculate CL intensity versus depth data for comparison with experiment (e.g. see line plots of calculated CL intensity data in Fig. 4(a) (b) and (c)). A variety of defect depth distribution profiles including uniform, step, Gaussian, exponentially decreasing, linearly decreasing, and half Gaussian functions were tested. In all cases the CL intensity approaches zero at non-zero energy due to the presence of an optically inactive or "dead layer".[36] The dead layer can arise from the reduced concentration of luminescent defects and/ or increased concentration of competitive non-radiative centers in the near surface region. The dead layer may result from polishing damage, surface related asymmetry which reduces the recombination of electron hole pairs (exciton recombination), and non-radiative recombination associated with surface impurities, oxides etc.

The CL integrated emission intensity versus electron beam energy data from the unirradiated specimen in Fig. 4(a) have been fitted with a uniform depth distribution of pre-existing defects with dead layer of 100nm, as shown in Fig 4(d). The equivalent data from the laser damaged specimens are significantly different from the unirradiated specimen. The data from the laser damaged specimens is inconsistent with uniform or step profiles or defect profiles which maximize at some depth below the surface. While it is not possible to determine the exact defect distribution profiles with data of this resolution, iterative fitting clearly shows that the maximum concentration of defects resulting from the laser induced damage is found at the surface, consistent with damage initiation at the surface. Fitting of a half Gaussian type profile with the maximum at the surface is consistent with all laser induced defect depth distributions observed. Iterative fitting also confirms the presence of a thin dead layer at the surface in all cases. The concentration of laser damage induced defects continuously decreases within the specimen, extending to a maximum depth of ~10μm. The majority of the laser damage induced defects are found within the first ~5μm. For example, in Fig. 4(e) and (f), modified half Gaussian depth defect distribution profiles have been fitted to the experimental data in Fig. 4(b) and (c) respectively. Note in Fig. 4(e) and (f), the concentrations of the laser induced defects associated with the 1.9eV and 2.7eV emissions, decrease as a function of depth to the pre-irradiation defect concentration levels, consistent with the pre-irradiation concentrations in Fig. 4(d). The iteratively fitted dead layer thicknesses of the laser damaged fused silica are ~300nm. It is noted that the dead layers are significantly thicker in the laser damaged regions than in the undamaged fused silica. This is likely to be due to the laser induced changes in the surface

morphology and increase in the concentration of non-radiative defect centers particularly in these damaged near-surface regions.

A compaction layer, approximately 10 μm thick and approximately 20% higher in density has been experimentally identified using x-ray tomography.[12] In addition macro- (10-0.1 μm) and micro-cracks (200-20 nm) have been found using high resolution Transmission Electron Microscopy (TEM).[12] It is noted that the range of electrons in 20% compacted fused silica is ~85% of the range in the original material. Conversely however, electron transport may be enhanced along cracks resulting in an increased electron range. These competing factors associated with the damage crater morphology introduce a degree of uncertainty in the maximum damage depth, estimated by CL microanalysis to be 10.0 ± 1.5 μm. The spatially resolved CL data is consistent with damage initiation at the exit surface, in agreement with other studies where it has been determined, that surface imperfections resulting from residual polishing contamination are associated with damage initiation.[9,12] The concentration of 355 nm laser induced defects is greatest near the damaged surface and continuously decays to pre-irradiation levels at maximum depth ~10μm below this surface. Following damage initiation, the catastrophic breakdown of the fused silica optics occurs with the damage increasing ~exponentially with each additional pulse.[37] CL microanalysis of the defect distribution associated with 355nm laser irradiation of more than a few pulses is limited by the spatial extent and non-uniformity of the catastrophic damage. For collection areas greater than ~200μm in diameter, the spatial response of the CL paraboloidal mirror is no longer linear due to its focusing characteristics and therefore contribution from damage craters on the periphery of the irradiated area will be underestimated.

Damage mitigation via CO_2 laser processing

Techniques for inhibiting the growth of 355 nm laser-induced surface damage on fused silica have previously been investigated including wet chemical etching, cold plasma etching, CO_2 laser processing, and micro-flame torch processing.[10] The technique that has been found to be most consistent and effective at stopping the growth of the laser damage on the exit surfaces of the fused silica optics is the CO_2 laser processing technique.[10,11] The pre-initiated damage sites are exposed to single pulses of a CO_2 laser to locally treat the laser damage, altering it such that the damage does not propagate further during subsequent irradiation with 355 nm laser pulses.[38]

CL microanalysis has been used to (i) identify the defects and (ii) determine the defect distribution associated with damage mitigated sites on fused silica: A laser damage site was pre-initiated on fused silica with a single 355 nm laser pulse at 45 Jcm^{-2}. This site was then treated with cw CO_2 laser photons of 10.6 μm for one second at a power level of 37.5 Watts with a beam diameter of 1.5 mm at the surface. Subsequently the fused silica was irradiated with the 355nm laser at 12 Jcm^{-2} for 1000 pulses at a repetition rate of 10Hz. The resultant damage mitigated site is characterized by a smooth low aspect ratio (~750μm diameter, ~15μm deep) pit. There is no apparent cracking or fiber formation resulting from thermal explosion of molten silica, as is the case when the fused silica is irradiated with 355 nm laser photons without processing to mitigate the damage. The damage morphology of the pit results in much less distortion and deflection of the laser beam than the multiple damage craters produced by laser irradiation without the benefit of the CO_2 laser damage mitigation processing. This is a very desirable outcome.

The damage mitigated pit resulting from (the initiation, mitigation processing, and subsequent laser irradiation) has also been investigated using non-destructive depth resolved CL microanalysis.

The CL from the damage mitigated pit is ~uniform with CL monochromatic imaging consistent with a uniform distribution of defects across the diameter of the ~750μm pit. CL emissions are observed at 1.9 eV, 2.3 eV, and 2.7 eV (See Fig. 6(a)). These emissions have also been observed from the 355 nm damage sites (see Figs. 1-5) as reported above and as before, are associated with non-bridging oxygen hole centers (NBOHC), self trapped excitons (STE) possibly with E' precursors (see previous discussion) and oxygen deficient centers (ODC) respectively. In addition, a low intensity previously unreported CL emission is observed from the damage mitigated pit at 3.2eV in CL data excited with electron beam with energy <10keV. This indicates that the defect associated with the 3.2eV emission is located near to the surface of the fused silica. It is noted that photoluminescence emission has been observed at ~3.1eV from silica, and attributed to an oxygen deficient defect center.[39-42] Luminescent emission has also been reported between 3.1-3.25eV from SiO_2 and has been attributed to the recombination of a hole trapped adjacent to a substitutional charge compensated aluminum - alkali ion center (Al^{3+} - M^+), (see Stevens-Kalceff[20] and references therein). The Al^{3+} substitutes for Si^{4+} thus requiring charge compensation, (M^+) which in ultra pure hydrated fused silica specimens[15] is most likely to be H^+. Kozlowski et al[9] have profiled contamination from polishing compounds extending ~200nm into the fused silica. Aluminum concentrations of up to 1000 parts per million (ppm) have been detected and attributed to residue from the final step in the polishing process involving Al_2O_3.[9] It is possible that some of the

aluminum may have been incorporated as a substitutional (Al – H) defect into the fused silica as a result of the 1000 high fluence UV laser pulses. Note also that the 3.2 eV emission is sensitive to and attenuated by extended periods of electron beam irradiation. This is consistent with the dissociation via radiolysis of the hydrogen charge compensator from the substitutional Al.[20] Thus the 3.2 eV emission is likely to be associated with the polishing impurities incorporated into the fused silica surface by multiple 3ω, 355nm laser pulses.

The CL spectra have been collected with constant beam power from the laser damage mitigated pit as a function of incident beam energy. The integrated CL intensities of each emission are fitted with Gaussian components and are then plotted as a function of electron beam energy (e.g. see experimental scatter plots of CL intensity data in Fig. 6(b)). The depth distributions of associated defect centers can then be determined from this data with iterative fitting using Equation 1 (e.g. see fitted line plots of CL intensity data in Fig. 6(b)) A variety of defect depth distribution profiles were tested. The concentration of laser damage induced defects continuously decreases within the specimen, to a maximum depth of ~6μm. The majority of the laser damage induced defects are found within the first ~3μm and the concentrations of the laser induced defects associated with the 1.9eV and 2.7eV emissions decrease as a function of depth to the pre-irradiation defect concentration levels, consistent with the pre-irradiation concentrations in Fig. 4(d). The iteratively fitted dead layer thicknesses of the laser damage mitigated fused silica are ~200nm. It is noted that the dead layers are significantly thicker in the laser damage mitigated regions than in the undamaged fused silica (~100nm) but less than the 355 nm laser damaged fused silica (~300nm). This is

likely to be due to the annealing of defect centers in these damaged near-surface regions and the resultant smoother surface morphology. Despite 1000 3ω, 355nm laser pulses the defect concentrations observed in the CO_2 laser processed fused silica are of the same order as in the unprocessed fused silica specimen after only a couple of pulses. CL microanalysis shows that in comparison with the 355 nm laser damaged fused silica, the defect generation in CO_2 laser processed fused silica is less and also the distribution of defects extends to a depth of 6.0 ± 1.0 μm rather than 10.0 ± 1.5 μm. CL microanalysis confirms that CO_2 laser processing of fused silica is very effective in mitigating the 355nm laser generation of point defects in the near surface region of fused silica.

Conclusions

Cathodoluminescence (CL) microanalysis has been used to (i) identify point defects induced in fused silica by high fluence 3ω, 355nm laser pulses following damage initiation and after damage mitigation (CO_2 laser processing) and has been used to (ii) nondestructively determine the spatial distribution of these defects. The CL emissions are observed at 1.9eV, 2.2eV, 2.7eV, 3.2eV and 4.4eV, and have variously been identified with the NBOHC (non-bridging oxygen hole center), an ODC (oxygen-deficient center), substitutional (Al-H) impurity centre resulting from residual impurities from polishing processes, and the STE (self-trapped exciton). The enhancement of the STE emission from the laser damaged sites is likely to be associated with the electron beam induced annealing of the E′ centers generated by the 355 nm laser irradiation.[13] The observed CL emissions and proposed identifications are summarized in Table 1. The spatially resolved CL data is consistent with damage initiation at the exit surface. The concentration of 3ω, 355 nm laser induced defects is greatest at the surface and monotonically decays to pre-

irradiation levels at ~10 μm depth below the surface. With CO_2 processing to mitigate damage, the defect concentration and distribution is reduced to a maximum depth of ~6μm. CL microanalysis confirms that CO_2 laser processing mitigates the 355nm laser generation of point defects in fused silica. CL microanalysis provides a sensitive, spatially resolved and nondestructive method of assessing the magnitude and submicron distribution of irradiation induced damage in technologically important materials including fused silica.

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Figures

Figure captions

Fig. 1. Typical visible CL spectra from fused silica: (a) undamaged area, and 3ω damaged area, (b) 30 Jcm^{-2}, 1 pulse, (c) 30 Jcm^{-2}, 2 pulses and (d) 45 Jcm^{-2}, 1 pulse. Gaussian emission components are indicated by arrows. CL data was collected with sampling area of 150 x 200 μm^2, and electron beam energy and current of 25 keV and 1.5 nA.

Fig. 2. (a) Secondary electron image (topography) of damage craters produced on the exit surface of SiO_2 by a pulse of 3ω, 355 nm laser photons at 45 Jcm^{-2}. The damage crater arrowed in (a) is shown at higher magnification in (b). The secondary electron image (b) is compared with corresponding panchromatic CL images excited by a (c) 15keV electron beam and a (d) 25keV electron beam. Note that the contrast has been reduced in (c) relative to (d) to avoid saturation in the center region of the crater. The secondary electron image of the center of damage crater (e) is compared with the corresponding CL image (f). CL emission is observed from the fibers (e.g. see arrows) resulting from the 355 nm laser induced thermal explosion which confirms these fibers consist of oxygen deficient silica.

Fig. 3. (a) Typical visible CL spectra collected for different incident electron beam energies and constant beam power from an exit surface damage site of fused silica irradiated with 355 nm laser (30 Jcm^{-2}, 2 pulses). (b). Typical componentized CL

spectrum (beam energy, 20 keV; beam current, 1.85 nA) from 355 nm laser irradiated fused silica (30 Jcm^{-2}, 2 pulses). The scatter plot shows the experimental data, the dashed line plots show the fitted Gaussian components (see text), and the solid line plot shows the sum of the fitted Gaussian components for comparison with the experimental scatter plot.

Fig. 4. Experimental (scatter plots) and calculated (line plots) integrated CL emission intensities from (a) undamaged, (b) laser damaged fused silica (355 nm, 30 Jcm^{-2}, 1 pulse) and (c) laser damaged fused silica (355 nm, 30 Jcm^{-2}, 2 pulses). Corresponding iteratively fitted defect depth distributions from (d) undamaged, (e) laser damaged fused silica (355 nm, 30 Jcm^{-2}, 1 pulse) and (f) laser damaged fused silica (30 Jcm^{-2}, 2 pulses). The error bars indicate the errors in the fitting only.

Fig. 5. (a) Electron Energy Transfer Function for fused silica, ρ = 2.2 gcm^{-3}. (b) The maximum penetration depth of normal incidence electrons into fused silica.[36]

Fig. 6. (a) Typical componentized CL spectrum (beam energy, 7 keV; beam current, 5.3 nA) from the exit surface damage site of 355 nm laser irradiated fused silica. The scatter plot shows the experimental data, the dashed line plots show the fitted Gaussian components (see text), and the solid line plot shows the sum of the fitted Gaussian components for comparison with the experimental scatter plot. (b) Experimental (scatter plots) and calculated (line plots) integrated CL emission intensities from laser damaged fused silica (355 nm, 30Jcm^{-2}, 1 pulse, CO_2 laser processing, 355nm, 12 Jcm^{-2}, 1000 pulses) and (c) corresponding iteratively fitted depth distribution of each defect.

Tables

Table 1

CL Emission (eV)			FWHM (eV)	associated defect centers
un-irradiated	**3w**	**3w+CO_2**		
1.9	1.9	1.9	0.17	NBOHC
-	2.3	2.3	0.40	STE (E' precursor induced by 3ω laser)
2.7	2.7	2.7	0.35	ODC
-	-	3.2	0.85	ODC and/or (Al - H) center
-	4.4	-	0.40	ODC

Table caption

Table 1

Comparison of CL emissions observed from unirradiated fused silica, 355nm laser irradiated fused silica without (3ω) and with CO_2 laser processing (3ω+CO_2) for damage mitigation. See text for details.

References

[1] H. Hosono and K. Kawamura, in *Defects in SiO_2 and Related Dielectrics: Science and Technology*, eds. G. Pacchioni, L. Skuja, and D. L. Griscom (Kluwer Academic, Boston, 2000), p. 213.

[2] *Laser-Induced Damage in Optical Materials Vol.*, (SPIE Proceedings 1999-2003).

[3] *Laser-Induced Damage in Optical Materials: 2002*; *Vol. 4679*, eds G. J. Exarhos, A. Guenther, M. Kozlowski, K. Lewis, and M. Soileau (SPIE Proceedings, 2002).

[4] H. Hosono, M. Mizuguchi, H. Kawazoe, and T. Ogawa, Applied Physics Letters **vol.74, no.19,** 2755 (1999).

[5] K. Kajihara, Y. Ikuta, M. Hirano, and H. Hosono, Applied Physics Letters **vol.81, no.17,** 3164 (2002).

[6] E. M. Campbell, Fusion Technology **26,** 755 (1994).

[7] C. Seifa and D. Malakoff, Science **289,** 1126 (2000).

[8] M. R. Kozlowski, R. Mouser, S. Maricle, P. Wegner, and T. Weiland; *Vol. 3578* (SPIE Proceedings, 1999), p. 436.

[9] M. R. Kozlowski, J. Carr, I. D. Hutcheon, R. Torres, L. M. Sheehan, D. W. Camp, and M. Yan; *Vol. 3244* (SPIE Proceedings, 1997), p. 365.

[10] L. W. Hrubesh, M. A. Norton, W. A. Molander, E. E. Donohue, S. M. Maricle, B. Penetrante, R. M. Brusasco, W. Grundler, J. A. Butler, J. Carr, R. J. Hill, L. Summers, M. D. Feit, A. M. Rubenchik, M. H. Key, P. J. Wegner, A. K. Burnham, L. A. Hackel, and M. R. Kozlowski, *Vol. 4679* (SPIE Proceedings, 2001), p. 23.

[11] R. M. Brusasco, B. Penetrante, J. A. Butler, and L. W. Hrubesh, *Vol. 4679* (SPIE Proceedings, 2001), p. 40.

[12] J. Wong, D. L. Haupt, J. H. Kinney, J. Ferriera, I. D. Hutcheon, S. G. Demos, and M. R. Kozlowski, *Vol. 4347*, (SPIE Proceedings, 2000), p. 466.

[13] M. A. Stevens-Kalceff, A. Stesmans, and Joe Wong, Applied Physics Letters **80,** 758 (2002).

[14] B. G. Yacobi and D. B. Holt, *Cathodoluminescence Microscopy of Inorganic Solids.*, (Plenum Press, New York, 1990).

[15] *See http://hpfs@corning.com/ for #7940 product specification* (Corning, NY, USA).

[16] L. Sheehan, S. Schwartz, C. Battersby, R. Dickson, R. Jennings, J. Kimmons, M. Kozlowski, S. Maricle, R. Mouser, M. Runkel, and C. Weinzapfel; *Vol. 3578* (SPIE Proceedings, 1998), p. 302.

[17] N. L. Boiling, M. D. Crisp, and G. Dube, Applied Optics **12,** 650 (1973).

[18] A. Palma, J. A. Lopez-Villanueva, and J. E. Carceller, J.Electrochem.Soc. **143,** 2687 (1996).

[19] M. A. Stevens-Kalceff and M. Phillips, Phys.Rev.B. **52,** 3122 (1995).

[20] M. A. Stevens-Kalceff, Physical Review B. **57,** 5674 (1998).

[21] M. A. Stevens-Kalceff, M. Phillips, A. R. Moon, and W. Kalceff, in *Cathodoluminescence in the Geosciences*, eds. M. Pagel, V. Barbin, P. Blanc, and D. Ohnenstetter (Springer-Verlag, Berlin, 2000).

[22] M. A. Stevens-Kalceff, Physical Review Letters **84,** 3137 (2000).

[23] *Defects in SiO_2 and Related Dielectrics: Science and Technology*, eds. G. Pacchioni, L. Skuja, and D. L. Griscom (Kluwer Academic, Boston, 2000).

[24] N. Matsunami and H. Hosono, Physical Review B **60,** 10616 (1999).

[25] L. Skuja, Journal of Non-Crystralline Solids **239,** 16 (1998).

[26] D. L. Griscom, J. Ceramics Soc. Japan **99,** 923 (1991).

[27] D. L. Griscom, Reviews of Solid State Science **4,** 565 (1990).

[28] K. S. Song and R. T. Williams, *Self-Trapped Excitons* (Springer-Verlag, Berlin, 1992).

[29] L. Skuja, J.Non.Cryst.Sol. **179,** 51 (1994).

[30] L. Skuja, in *Defects in SiO_2 and Related Dielectrics: Science and Technology*, eds. G. Pacchioni, L. Skuja, and D. L. Griscom (Kluwer Academic, Boston, 2000), p73.

[31] T. E. Tsai, D. L. Griscom, and E. J. Friebele, Phys.Rev.Lett. **61,** 444 (1988).

[32] V. B. Sulimov and V. O. Sokolov, J.Non-Cryst.Sol. **179,** 260 (1994).

[33] S. Hayashi, K. Awazu, and H. Kawazoe, J.Non-Cryst.Sol. **179,** 235 (1994).

[34] L. Skuja and B. Guttler, Physical Review Letters **77,** 2093 (1996).

[35] M. Feit, L. Hrubesh, A. Rubenchik, and J. Wong, *Vol. 4347*, (SPIE Proceedings, 2001), p. 316.

[36] M. Goldberg, T. Barfels, and H. J. Fitting, Fresenius Journal of Analytical Chemistry **361,** 560 (1998).

[37] P. R. Bouchut, L. Delrive, D. Decruppe, and P. Garrec, *Vol. 5252*, (SPIE Proceedings, 2003).

[38] M. Feit and A. Rubenchik, *Vol. 4932*, (SPIE Proceedings, 2002), p. 91.

[39] L. Skuja, J.Non.Cryst.Sol. **149,** 77 (1992).

[40] R. Tohman, Y. Mizuno, K. Ohki, K. Sasagane, K. Nagasawa, and Y. Hama, Phys.Rev.B. **39,** 1337 (1989).

[41] A. Anedda, C. M. Carbonaro, F. Clemente, and R. Corpino, Journal of Applied Physics **92,** 3034 (2002).

[42] M. Leone, R. Boscaino, M. Cannas, and F. M. Gelardi, J Non-Cryst. Solids **216,** 105 (1997).