Green luminescence in silica glass: A possible indicator of subsurface fracture

Jessica Fournier, Jérôme Neauport, Pierre Grua, Evelyne Fargin, Veronique Jubera, David Talaga, Stéphane Jouannigot

Green luminescence in silica glass: A possible indicator of subsurface fracture

Jessica Fournier, Jerome Neauport, Pierre Grua, Evelyne Fargin, Véronique Jubera, David Talaga, and Stéphane Jouannigot

Citation: Appl. Phys. Lett. **100**, 114103 (2012);
View online: https://doi.org/10.1063/1.3693393
View Table of Contents: http://aip.scitation.org/toc/apl/100/11
Published by the American Institute of Physics

Green luminescence in silica glass: A possible indicator of subsurface fracture

Jessica Fournier,[1,2] Jerome Neauport,[1,a)] Pierre Grua,[1] Evelyne Fargin,[2] Véronique Jubera,[2] David Talaga,[3] and Stéphane Jouannigot[4]
[1]*Commissariat à l'énergie atomique, Centre d'études scientifiques et techniques d'Aquitaine, BP 2, F-33114 Le Barp, France*
[2]*CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr. A. Schweitzer, Pessac F-33608, France*
[3]*Institut des Sciences Moléculaires, UMR 5255 CNRS, Université de Bordeaux 1, 351 Cours de La libération, 33405 Talence cedex, France*
[4]*Laboratoire des Composites Thermo-Structuraux, 3 Avenue de la Boetie, 33600 Pessac, France*

(Received 2 December 2011; accepted 21 February 2012; published online 12 March 2012)

We investigate the nature of defects triggering laser damage in fused silica in subsurface fractures in nanosecond near ultraviolet regime. Mechanical, laser induced surface flaws as well as pristine silica surface were characterized by optical microscopy and luminescence confocal microscopy before and after acid etching. In all cases, photoluminescence decreases with etching time assessing the existence of defects close to the surface. Spectral analysis of the evolution of these signals during etching allows new interpretations of the nature of precursors inducing damage. Green luminescence around 2.25 eV is seen as a potential subsurface fracture indicator leading to laser damage. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3693393]

The performances of large inertial fusion laser facilities are currently limited by the propensity of fused silica optics to damage under high fluences with a wavelength of 351 nm. Damage initiates in the form of micro craters with diameters ranging from 10 to 100 micrometers. Since damage size grows exponentially when submitted to additional laser shots, the optical lifetime can become rather limited. Significant progress has been made to reduce the damage density of fused silica optics by modifying the polishing processes,[1] limiting surface impurities,[2] reducing subsurface damage,[3] or developing the surface post treatment.[4] Nevertheless, and in spite of these improvements, the real physical nature of damage precursors stays quite vague. Fused silica is used as raw material for laser optics operating in transmission due to its low absorption, high index uniformity, and high laser induced damage threshold in the ultraviolet. Fused silica's damage threshold for 3 ns pulses drops down to some tenth of J/cm^2 for the best polishing processes.[1] Such a behavior supports the fact that damage is induced by precursors present in the subsurface regions.

From a macroscopic point of view, subsurface fractures are recognized to be possible damage precursors, and their removal induces an increase of the laser damage threshold.[4] Since detection of such subsurface defects is difficult on polished parts, authors decided to use indentation induced flaws as a representative tool to understand how damage is triggered at wavelength of 351 nm. Using this principle and a confocal time resolved PL imaging system, Laurence *et al.* showed that indentations exhibit a luminescent signal above 550 nm for a 400 nm excitation wavelength.[5] Miller *et al.* demonstrated that this luminescence signal is drastically decreased by removing a thin layer (~200 nm) via acid etching, and that such a decrease was accompanied by an improvement of damage threshold,[6] coherent with previous experiments on optical silica surfaces.[4] In the present work, we propose to use a similar approach by studying the evolution of PL via spectral analysis, on indentation fracture flaws and pristine silica both before and after etching. Our aim is to get a better knowledge of the physical nature of defects triggering laser damage in subsurface fractures.

Experiments were conducted on 50 mm diameter—5 mm thick high purity super polished Corning 7980 fused silica samples, of which the finishing processes ensured a low content of photoactive impurities, such as cerium compounds.[2] Before measurements, all the samples were thoroughly cleaned in order to prevent external contamination on studied surfaces which could interact with the excitation radiation and thus bias the measurements.[7] Indentations were created using a diamond sphero-conical tip with a 20 μm diameter; the load was applied during 60 s with a force of 1.5 N.[7] After making the indentation surface flaws, samples were etched using a HF/HNO_3 solution with 80% vol. of HF and 20% vol. of HNO_3.[2] The removed thickness was about 6 μm in order to suppress most defects. PL spectra were carried out on a LABRAM HR-800 spectrometer, a high resolution Raman spectrometer with luminescence confocal microscopy capabilities. Excitation was performed at 3.81 eV (325 nm) by the use of a continuous He/Cd laser at room temperature. The focal spot size on the sample was about 1 μm^2 with a maximum available power of about 10 mW. The signal was collected on a CCD camera and the spatial resolution of the spectrometer was about 1 μm. The pinhole was opened at 300 μm due to the weakness of the PL signal emitted by the samples. For all measurements, the obtained spectra were corrected by the response function of the spectrometer.

The luminescence spectra obtained on pristine fused silica surfaces before and after acid etching are shown in Fig. 1. Both spectra yielded a broad luminescence peak

a)Author to whom correspondence should be addressed. Electronic mail: jerome.neauport@projet-lmj.org.

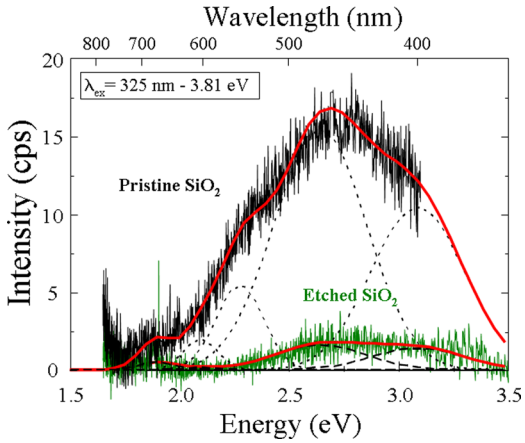

FIG. 1. (Color online) Comparison of spectra obtained for pristine silica and etched silica (100 μW laser power). The dotted line curves represent the Gaussian components of the signals.

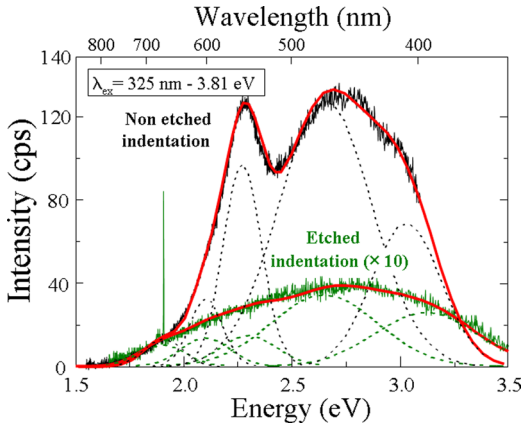

FIG. 2. (Color online) Comparison of photoluminescence under 3.81 eV excitation for non etched (10 μW laser power) and etched indentation (1 mW laser power). The spectrum of etched indentation is enlarged by a factor 10 in order to show its Gaussian components. Signal of etched indentation is e.g., about 30 times stronger than the one of etched surface shown on Figure 1.

around 2.75 eV, but an important decrease of PL intensity occurred for etched silica surface with respect to the non-etched one. For comparison purposes, spectra have been deconvoluted into the five Gaussian components centered at 1.90 eV, 2.10 eV, 2.25 eV, 2.65 eV, and 3.10 eV (Table I) in agreement with previous experiments on silica glass surface flaws.[5,6] Spectral analysis brings additional information. First, etching does not appear to create new kinds of luminescent defects in the 1.5-3 eV range, since in this spectral domain, deconvolution is performed by using the same Gaussian components for etched and non-etched silica. Second, the 2.1 and 2.25 eV bands have effectively disappeared from the etched silica spectrum (Table I). In the spectral range beyond 3 eV, due to the high level of noise and weak signal, an accurate Gaussian deconvolution remains tentative; however that may be, the PL intensity is strongly reduced by etching.

Spectra obtained on an indentation before and after acid etching are presented in Fig. 2. As for pristine silica, a strong decrease of signal is evident. Moreover, we can again see a broad luminescent signal centered around 2.75 eV on the etched indentation. The five Gaussian bands utilized for the deconvolution of PL spectra are initially centered at around 1.90 eV, 2.10 eV, 2.25 eV, 2.65 eV, and 3.10 eV (Table II) as for pristine silica glass and allowed to slight shift in optimizing the deconvolution.[6] On a non-etched indentation spectrum, an intense and narrow band peaks around 2.25 eV. After etching, the band which appears at the same energy has a larger width and much weaker intensity. It appears clearly that the majority of defects responsible for the narrow band around 2.25 eV in the indentation were located within the 6 μm layer removed by etching, likely due to the presence of subsurface microcracks. The microscopy image of the etched indentation zone and the PL intensity mapping carried out at 2.25 eV in the same zone are presented in Fig. 3. The PL intensity is shown to be shifted off-center, as compared to the image of the indentation trace, likely due to the randomly fractured area existing below the surface flaw, as already observed by Miller *et al.*[6]

What kind of defects could exhibit such luminescence properties? In fused silica, the most common structural defects are the oxygen deficient center (ODC) and the non bridging oxygen hole center (NBOHC),[8] but such defects are known to exhibit a very low absorption at 351 nm (3.53 eV). The 1.9 eV band is well known and attributed to NBOHC, while the 2.65 eV long lifetime luminescence (10.2 ms) is ascribed to ODC(II) defect.[8] Other defects emit around 2.65 eV but with a short lifetime luminescence (~3 ns), likely silicon clusters.[9] Presently, the ~3 eV bands interpretation still gives rise to much controversy,[8–10] but this subject lies beyond the scope of this letter. Bands peaking around 2.2 eV have already been detected in γ-irradiated silicas,[10,11] showing strong similarities with the present work.

TABLE I. Gaussian band parameters obtained for luminescence spectrum of pristine silica: energy position and FWHM. The intensities integrated over each band, obtained before and after etching, are also reported.

		Integrated intensity (arb. units)	
Energy (eV)	FWHM (eV)	Non etched	Etched
1.90	0.19	0.40	0.10
2.10	0.18	0.38	0[a]
2.28	0.25	1.46	0[a]
2.65	0.50	8.22	0.84
3.10	0.50	5.57	0.74

[a]value well below the noise amplitude.

TABLE II. Gaussian band parameters obtained for luminescence spectra of etched and non etched indentation: energy position, FWHM, and integrated intensities over each band.

Non etched intendation			Etched intendation		
Energy (eV)	FWHM (eV)	Integ. Intens. (arb. units)	Energy (eV)	FWHM (eV)	Integ. Intens. (arb. units)
1.90	0.21	2.9	1.90	0.25	0.24
2.10	0.18	6.1	2.10	0.26	0.33
2.27	0.21	21.4	2.30	0.30	0.41
2.66	0.52	68.8	2.63	0.57	1.85
3.04	0.38	27.4	3.12	0.55	1.34

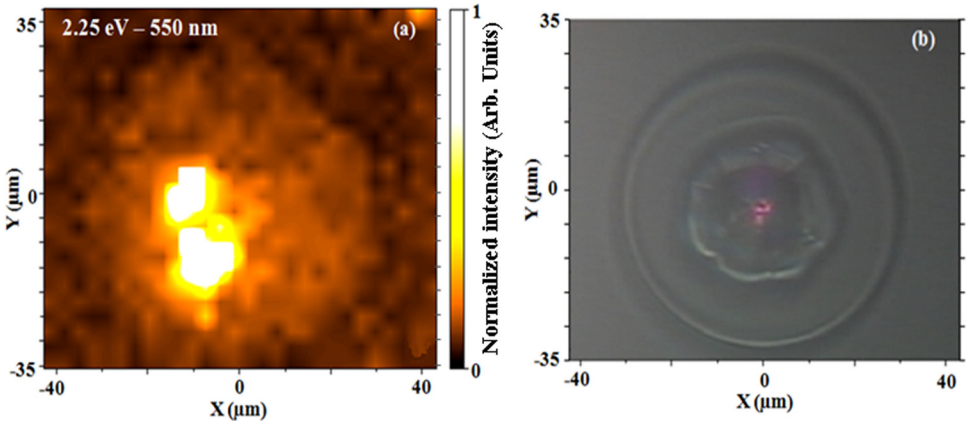

FIG. 3. (Color online) (a) Photoluminescence cartography for 2.25 eV emission obtained on etched indentation under 3.81 eV excitation. (b) Transmission microscopy image of the indentation.

In oxygen-surplus silica glass,[10] a band centered at 2.24 eV with a 0.19 eV full width at half maximum (FWHM) is observed, while in oxygen-deficient silica,[11] a broader band (0.32 eV) peaking at 2.10 eV is found. In the case of the 2.24 eV band, authors had proposed to attribute the band to peroxy radical or peroxy linkage, but with the help of our recent calculations,[12] we have been able to rule out such hypotheses and rather suggest the involvement of O_2^- ions.[13] In the case of the 2.10 eV band, the luminescence was ascribed to E_δ' defects, a hypothesis also supported by our calculations[12] and other authors.[14] Hence, the 2.10–2.25 eV luminescence bands observed in non-etched indentation may be attributed to interstitial O_2^- ions trapped in subsurface microfractures in the vicinity of E_δ' centers with positive charge compensating the O_2^- ion. Complementary photo bleaching experiments at 325 nm were carried out on non-etched indentations. In these experiments, the PL signals were gradually changing from the characteristic type shown in Fig. 2 (non-etched indentation) towards a pristine silica spectrum, which is also analogous to the one of etched indentations. This emphasizes the fact that defects which emit around 2.25 eV are the most sensible to neutralization by an ultraviolet long term irradiation.

The 2.25 eV luminescence band's interpretation is consistent with the observed change of luminescence signal after etching. As the indentation is subjected to acid etching cracks are enlarged, leading to a modification of the defect distribution, due first to the action of acid solution and second to the presence of atmospheric species, which facilitate the surface rebuilding. Consequently, the 2.25 eV band appears as a relevant indicator of the silica glass fragility under 351 nm laser irradiation, since it constitutes a signature of non emerging subsurface microfractures.

We would like to thank C. Ambard for sample etching. This work is supported by the Conseil Régional d'Aquitaine and is performed in the framework of the Etude et Formation en Surfacage Optique (EFESO) project and of the Laser Interaction and New Optical Functionality (LasINOF) group.

[1]J. A. Menapace, B. Penetrante, D. Golini, A. F. Slomba, P. E. Miller, T. G. Parham, M. Nichols, and J. Peterson, Proc. SPIE **4679**, 56 (2002).
[2]J. Néauport, P. Cormont, L. Lamaignère, C. Ambard, F. Pilon, and H. Bercegol, Opt. Commun. **281**, 3802 (2008).
[3]T. Suratwala, L. Wong, P. Miller, M. D. Feit, J. Menapace, R. Steele, P. Davis, and D. Walmer, J. Non-Cryst. Solids **352**, 5601 (2006).
[4]T. I. Suratwala, P. E. Miller, J. D. Bude, W. A. Steele, N. Shen, M. V. Monticelli, M. D. Feit, T. A. Laurence, M. A. Norton, C. W. Carr *et al.*, J. Am. Ceram. Soc. **94**, 416 (2010).
[5]T. A. Laurence, J. D. Bude, N. Shen, T. Feldman, P. E. Miller, W. A. Steele, and T. Suratwala, Appl. Phys. Lett. **94**, 151114 (2009).
[6]P. E. Miller, J. D. Bude, T. I. Suratwala, N. Shen, T. A. Laurence, W. A. Steele, J. Menapace, M. D. Feit, and L. L. Wong, Opt. Lett. **35**, 2702 (2010).
[7]J. Fournier, J. Néauport, P. Grua, V. Jubera, E. Fargin, D. Talaga, and S. Jouannigot, Opt. Express **18**, 21557 (2010).
[8]L. Skuja, J. Non-Cryst. Solids **239**, 16 (1998).
[9]H. Nishikawa, R. E. Stahlbush, and J. H. Stathis, Phys. Rev. B **60**, 15910 (1999).
[10]Y. Sakurai and K. Nagasawa, J. Appl. Phys. **86**, 1377 (1999).
[11]Y. Sakurai, J. Appl. Phys. **95**, 543 (2004).
[12]J. Fournier, Ph. D. dissertation, Université de Bordeaux I, Bordeaux 2011.
[13]J. Rolfe, J. Chem. Phys. **40** 1664 (1964); K. M. Ervin, I. Anusiewicz, P. Skurski, J. Simons, and W. C. Lineberger, J. Phys. Chem. A **107**, 8521 (2003).
[14]H. Nishikawa, E. Watanabe, D. Ito, Y. Sakurai, K. Nagasawa, and Y. Ohki, J. Appl. Phys. **80**, 3513 (1996).