Laser-induced microexplosion confined in a bulk of silica: Formation of nanovoids

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Laser-induced microexplosion confined in a bulk of silica: Formation of nanovoids

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We report on the nanovoid formation inside synthetic silica, viosil, by single femtosecond pulses of 30–100 nJ energy, 800 nm wavelength, and 180 fs duration. It is demonstrated that the void is formed as a result of shock and rarefaction waves at pulse power much lower than the threshold of self-focusing. The shock-compressed region around the nanovoid is demonstrated to have higher chemical reactivity. This was used to reveal the extent of the shock-compressed region by wet etching. Application potential of nanostructuring of dielectrics is discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2204847]

Formation of nanostructures inside transparent materials is gaining an interest due to potential applications in plasmonics, nanophotonics, three-dimensional (3D) optical memory,[1,2] and photonic crystals.[3,4] Particularly, the voids in solid transparent dielectrics (crystalline, inorganic glass, and polymers) can be created by a single[5] or multipulse[6] exposure by femtosecond pulses at high irradiance. The mechanism of void formation has been attributed to the self-focusing,[5] spontaneousness,[7] or self-formation;[8] however, the phenomenon has not been fully understood, e.g., no power dependence of a void size on pulse energy has been derived. The recorded structural 3D modifications, including voids, critically depend on self-focusing. Usually, when numerical aperture of the focusing lens is small NA<0.5 the power per pulse necessary to record photomodification in transparent medium exceeds that of self-focusing and linear damage line results. Similarly, the linear dotted damage line can be recorded by a single femtosecond pulse using high-NA (NA=0.8) objective lens[9] due to a nonlinear Gaussian-to-Bessel pulse/beam transformation.[10] It has been shown that once the nonlinear on-axis absorption becomes significant, it transforms the incoming Gaussian into the Bessel pulse,[10] and leads towards filamentation in glass.[11] The same mechanism of nonlinear axial absorption accounts well for self-action of Bessel pulse and can be used to record a dotted damage line with periodically spaced sites of photomodification.[12]

Here, we show that the nanovoid in glass is formed as a result of microexplosion which triggers shock and rarefaction waves. The nanovoid can be created by pulse which power is below the threshold of self-focusing. The scaling of the size of void and shock-compressed region on the absorbed energy have been derived and complies well with those experimentally measured.

In our experiments we used synthetic silica, viosil, which is transparent until 150 nm wavelength, has mass density of $\rho=2.2$ g/cm^3, and Young modulus $E=74.5$ GPa. Femtosecond pulses of 180 fs duration and 800 nm wavelength were tightly focused by an objective lens of numerical aperture, NA=1.35, at 10 μm depth. Inspection of the irradiated region was carried out by scanning electron microscopy (SEM) after sample was cleaved to observe a side view of the void and surrounding region. The extent of the photomodified (densified) region around the nanovoid was revealed by wet etching in aqueous solution of hydrofluoric acid (the details of this method can be found elsewhere[13,14]). The diameters of the void D_v, shock-affected D_a, and etched D_e regions were determined as the lateral cross sections with respect to the direction of irradiation (the axial cross sections of the photomodified regions were usually larger). The D_e diameter of etched out channel was measured when the irradiation bits were connected, while the $D_{v,a}$ were determined for the single bits.

The void was observed with a starting pulse energy of 40 nJ (at focus) as shown in Fig. 1, which corresponded approximately to the three thresholds of optically recognizable photomodification induced by a single laser pulse. At pulse energies higher than 85 nJ formation of cracks was observed (Fig. 2). To create an isolated cavity within a bulk solid, material has to be expelled from the void into a shell of compressed material to comply with mass conservation. Thus a pressure well in excess of the strength of material (the "cold" pressure, i.e., the Young modulus) should be created. To achieve this we focused the pulse of a standard femtosecond laser (~100 nJ, 180 fs, and 800 nm) into viosil using an oil-immersion objective lens with a high numerical aperture NA=1.35. The focal volume was 0.3 μm^3 and the area of the beam waist was 0.15 μm^2 [full width at half maximum (FWHM)] with corresponding maximum irradiance of 0.1 PW/cm^2 for the 100 nJ pulses. The pulse power was much lower than the threshold for self-focusing (~2 MW/pulse), therefore, the beam propagated without

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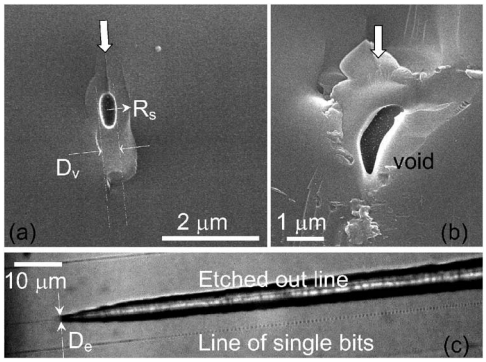

FIG. 1. The side-view SEM images of the axial cross section of the void recorded in viosil silica by single pulses of 40 (a) and 132 nJ (b) at 800 nm wavelength and 180 fs duration. The lateral radius where shock wave stopped is R_s (densified region); D_v is the lateral void diameter. The top-down arrows mark the direction of irradiation. Pulse energy is given at the focus; the threshold of optically observable damage was 13±2 nJ. (c) The phase-contrast Nomarski image showing enhanced etching rate along the line of bits formed by a single-pulse dielectric breakdown (see text for details).

causing any damage to the glass between the outer surface and the focal spot.

The void is surrounded by a densified shell; however, the diameter of this modified region was difficult to recognize in SEM images [Fig. 1(a)]. Also, after sample is cleaved, the void is not necessarily sliced at its largest cross section. The true extent of the densified region was revealed by wet etching.[14] The line of damage spots was recorded inside the viosil with a separation of approximately 200 nm and was etched in 5% aqueous solution of hydrofluoric acid. This method of determination of the extent of densified region was not very precise, since the highest etching rate contrast between the optically altered and unirradiated parts was approximately 40. Hence, the unaffected regions of viosil were etched as well altering the measured diameter of the densified part. This is illustrated in Fig. 1(c), where taper along the etched-out channel had developed. The intrabit distance in this case [Fig. 1(c)] was approximately 1.2 μm, the bits were recorded at approximately 90 nJ/pulse, and the diameter of channel, D_e, at its tip was ~1 μm. The diameter of the narrowest channels was revealed by confocal microscopy (360 nm resolution in our experiments) or by cleaving the sample and SEM observation as in the case of voids. Despite

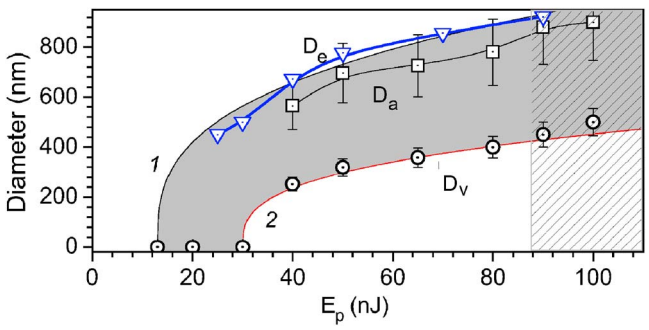

FIG. 2. (Color online) Dependence of the void's lateral diameter D_v, diameter of shock-affected region D_a, and diameter of channel wet etched in 5% aqueous solution of HF, D_e, on pulse energy E_p. Dashed area depicts conditions when cracks were observed around the void before cleaving. Theoretical fit dependencies (1,2) were calculated by Eqs. (1) and (2) respectively, with $E_{abs} \approx 0.6E_p$. Gray area depicts the densified region surrounding the void.

uncertainty of D_a determination, the etching procedure confirmed the presence of the densified, wet-etchable shell around the void. Figure 2 summarizes evaluation of diameter of the densified part D_a carried out by SEM and by wet etching D_e together with measurement of the void diameter D_v. In these experiments, the D_e was measured for the intrapulse separation of 200 nm, at which the fastest channel formation in the etchant was observed.[14]

At intensities 20–100 TW/cm^2 a small region within the focal volume was very rapidly ionized by the combined action of avalanche and multiphoton processes in only a few optical cycles creating multiply ionized solid-state density plasma.[2] The initially transparent silica was transformed into plasma with a skin depth of approximately 60 nm which effectively absorbs 60% of the incident energy creating, e.g., a pressure of 13 TPa (energy density of 13 MJ/cm^3) for a E_p =100 nJ pulse. We used the absorption coefficient of plasma 0.6 in all calculations. Such pressure is well in excess of the glass strength E=75 GPa. In these conditions a strong shock wave starts to propagate outside the region where the energy is deposited while the rarefaction waves simultaneously move inwards creating a void. The time for energy transfer from the electrons to ions and the time to establish local thermodynamic and ionization equilibria (~1 ps) as well as the pulse duration are much shorter than the characteristic hydrodynamic time of 1 ns (the onset of ion movement). The shock wave emerges at the boundary of the absorbing volume at ~2 ps. Therefore, the processes of void formation can be well described by equilibrium plasma hydrodynamics with instantaneous energy release in the absorbing volume. Computer simulations were performed in the spherical geometry using the hydrodynamic code CHIVAS (Ref. 15) and corroborated the proposed mechanism.[16] The size of the void and the shock-wave-affected (densified) region were determined experimentally as functions of the deposited energy [the latter from the size at the boundary between the compressed viosil and unaffected material as shown in the Fig. 1(a)] and are in quantitative agreement with simulations. The shock wave stops when the pressure behind the shock front becomes comparable with the strength (Young modulus) of the solid.

The formation of a void and densified zone can be understood from simple reasoning based on the laws of mass and energy conservation. Let us consider for simplicity spherically symmetric motion. The shock wave propagating in a cold material loses its energy due to dissipation, that is, due to the work done against the internal pressure (Young modulus) that resists material compression. The distance at which the shock front effectively stops defines the shock-affected volume. Actually at this point the shock wave converts into a sound wave, which propagates further into the material without inducing any permanent changes to the glass. This distance where the shock wave stops R_s can be estimated from the condition that the internal energy in the volume inside the shock front is comparable to the absorbed energy: $(4/3)\pi R_s^3 p_0 = E_{abs}$. In other words at this position the pressure p_0 behind the shock front equals the internal pressure E of the cold material.[17] One can reasonably suggest that the boundary observed between the densified (shock-compressed) and the unmodified (pristine) glass corresponds to the distance R_s, where the shock wave effectively stopped. The experimentally measured dependence of the laser-affected zone diameter, $D_a \approx 2R_s$, (outer size of shock-

compressed region) on the laser energy can be fitted using the above argument by the following formula:

$$D_a = l_a \sqrt[3]{E_{\text{abs}}}, \tag{1}$$

where l_a is measured in nanometers and E_{abs} is in nanojoules.

Similarly one can apply the mass conservation law to estimate the density of compressed material from the void size. Void formation inside a solid is only possible if the mass initially contained in the volume of the void was pushed out and compressed. Thus after the microexplosion the whole mass initially confined in a volume with diameter D_a resides in a spherical layer in between D_a and D_v, which has a density $\rho = \rho_0 \delta$ with $\delta > 1$. The void diameter can be expressed through the compression ratio and the diameter of laser-affected zone with the help of mass conservation as follows:

$$D_v = D_a \sqrt[3]{1 - 1/\delta}. \tag{2}$$

Typically we observed $D_v \sim 0.5 D_a$ which means that densified material has a density of 1.14 times higher than that of glass. The experimental data of void diameter were best fitted by Eq. (2) with $l_a = 65$ nm and the threshold pulse energy $E_p^{\text{th}} = 30$ nJ (see Fig. 2). The threshold pulse energy would correspond to the onset of void formation. The threshold of amorphous region formation was $E_p^{\text{th}} = 13$ nJ [Eq. (1)]. The absorption length $l_a = 65$ nm complies well with the ~ 60 nm skin depth of metallic state of ionized silica. Experimental results were fitted qualitatively well by the proposed theory, even the actual focal spot was elliptical, not spherical as implied in the derivation of Eqs. (1) and (2). This mechanism should help to understand photomodification processes and void formation in crystals[5] and plastics.[18–20]

Let us discuss the modifications of the shock-compressed region. It becomes wet etchable in aqueous solution of hydrofluoric acid[13,14] and has the higher density than surrounding silica (Fig. 2). The Si–O–Si angles become smaller inside the densified region, which makes the oxygen more exposed and reactive (a Lewis base mechanism). One of the consequences of the silica mass density increase is a refractive index augmentation, i.e., a polarizability increases, since the polarizability α_m is proportional to the refractive index n via the Lorentz-Lorenz relation

$$\alpha_m = \frac{3V_m}{4\pi N_A} \frac{n^2 - 1}{n^2 + 2}, \tag{3}$$

where V_m is the molar volume and N_A is the Avogadro number. Polarizability can be directly related to the optical basicity,[21] which is a phenomenological constant defining the chemical basicity (or acidity) of glasses. It was demonstrated that the optical basicity of complex multicomponent glasses can be calculated by the addition of the corresponding basicities of the constituent oxides multiplied by the corresponding weight factors.[21] An increased polarizability signifies the increased basicity (i.e., an enhancement of ionicity) and vice versa. It is possible to link the change of optical properties (refractive index) induced, e.g., by pulsed irradiation, to the chemical wet etching. The regions of silica with larger refractive index around the void become more basic (ionic) and, hence, show an enhanced etchability as compared with the unirradiated glass. In silica-based glasses, larger mass density is related to larger refractive index. Consequently, silica of higher mass density shows an increased chemical etchability, a kind of counter-intuitive finding confirmed experimentally.[14] Modified materials are expected to be formed in the "shocked" regions,[22–26] which opens alternative processing routes even for the most inert oxides.

In conclusion, the nanovoid formation has been explained as a result of shock and rarefaction waves inside the silica glass (viosil). The dimensions of the shock-compressed region and void scale with the absorbed energy as $D_{a,v} \sim \sqrt[3]{E_{\text{abs}}}$. The shock-compressed regions have altered physical and chemical properties, which helped to reveal the extent of shock-densified region by wet etching.

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