Photo-Induced Structural Changes in Glass

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This paper describes the application of femtosecond laser techniques to producing structural changes in transparent media, particularly various types of glasses, including soda lime and lead silicate glasses and chalcogenide glasses. Two processes that involve material ablation are investigated, deep-hole drilling in millimeter-thick materials and rapid micro-via or grating fabrication at the micron level. In addition we describe the fabrication of micron-scale optical waveguides in thin film photo-sensitive glasses by inducing structural changes that change the refractive index of the material.

1. Introduction

Femtosecond laser micromachining has become important in recent years for many fields including micro-optics, micro-electronics, micro-biology and micro-chemistry. Laser ablation, because of its non-contact nature, allows the micromachining and surface patterning of materials with minimal mechanical and thermal deformation. It is now well known that for many of these applications the femtosecond regime offers advantages over the nanosecond regime. These advantages lie in its ability to deposit energy into a material in a very short time period, before thermal diffusion can occur. As a result, the heat-affected zone, where melting and solidification can occur, is significantly reduced, leading to structured features that are smaller in size, have higher aspect ratios, and have greater spatial precision.

Another advantage of femtosecond laser micromachining is its versatility in the range of materials that can be processed. Femtosecond laser micro-machining is applicable to metals, semiconductors, polymers, oxide ceramics, silica aerogels, optical glasses and crystals, and lends itself to a variety of processing that include the fabrication of photonic crystals[1], data storage, fabrication of waveguides[2], gratings and single mode couplers.[3]

In this paper we describe three types of femtosecond laser processing in glasses. First, we describe deep hole fabrication in optical glasses and composite materials using mJ, 10 Hz–1 kHz, femtosecond lasers pulses. In this study we have identified new non-linear optical effects that modify the hole-drilling process. Second, we describe the use of MHz femtosecond laser pulses of only a few 10s of nJ energy for creating micron-scale surface relief features in glasses by ablative removal of material. This makes way for the fabrication of gratings and other surface relief structures for micro-electronics and biological engineering applications. Finally, femtosecond laser pulses, of a few 10's of nJ/pulse at high repetition rates (27 Mhz) are used to modify thin films of chalcogenide glass As_2S_3, creating optical waveguides that may well find numerous applications in the photonics industry.

2. Femtosecond laser ablation mechanisms

2.1 Basic processes

The mechanisms that govern femtosecond laser ablation can be complex, depending on the regime being used. In general the following takes place[4]: Bound and free electrons at the surface layer are excited via multi-photon absorption. Hot electrons are generated, the material becomes ionized and a plasma forms at the surface of the material. The energy is then transferred to the lattice through bond breaking and material expansion (**Figure 1**).

2.2 Advantages of the femtosecond regime

Since the processes described above occur on a picosecond time scale, thermal diffusion into the material is nearly negligible. The thermal relaxation is characterized by the thermal diffusion length D related to the

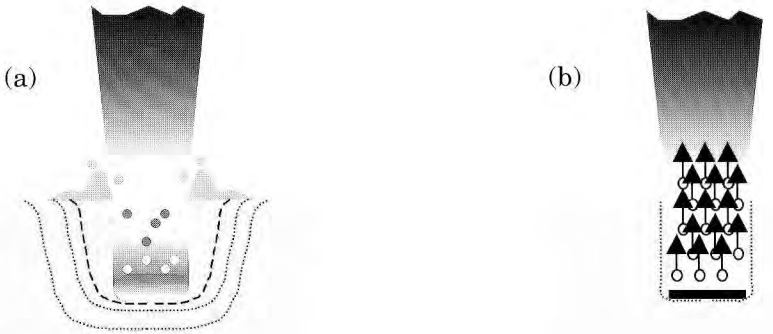

Figure 1 Schematic illustrating the difference between conventional (**a**) and femtosecond (**b**) micromachining.

pulse width τ_p by $D = \kappa\tau_p^{1/2}$, where κ is the thermal diffusivity of the material.[5] If D is shorter than the absorption length, the ablation precedes the thermal diffusion and the material does not have time to melt and resolidify. As a consequence, higher precision in structural micro-machining can be achieved.

In addition, in the nanosecond regime, it is generally accepted that ablation begins with the ionization of surface carriers, which are typically defects or impurities.[6] Due to the non-uniform distribution of surface carriers in dielectrics, experiments have demonstrated that no precisely-defined laser-induced damage threshold exists for laser pulses longer than 10 ps. By contrast, ultrashort laser pulses (<200 fs), with target intensities often in excess of 10^{12} W/cm^2, are capable of freeing bound electrons via Multi-Photon Ionization (MPI). Thus, experiments have shown that the laser-induced damage threshold of an ultrashort laser pulse has a precise value corresponding to the onset MPI, which is completely determined by the ionization bandgap energy of the target material.

The reasons above make femtosecond micromachining an attractive technique for the fabrication of fine surface structures in transparent materials. In this paper, we demonstrate that femtosecond laser pulses from a regeneratively amplified Ti:Sapphire can be used to drill holes (≥ 1 mm in depth) with high aspect ratio (≥ 10:1) in transparent materials at atmospheric pressure.

3. Deep hole drilling in silicate glasses

3.1 Experiment

We have investigated the laser ablation of two silicate glasses in three different laser ablation scenarios: with a femtosecond laser at 845 nm, with a nanosecond laser at 845 nm and with a nanosecond laser at 1064nm. To study the influence of the ionization bandgap on laser ablation, we use soda-lime glass (~5 eV) and 45%mol. PbO lead-silicate glass (~2.5 eV) as ablated materials.[7] The intent of these studies was to examine hole-drilling in the regime most likely to be of practical use, that is, at high intensities in an ambient air environment. Ablation is performed at atmospheric pressure in two regimes, below and above the air ionization threshold intensity, to gauge how air-ionization modifies the hole profile and material removal rate.

The femtosecond laser system is a Kerr-lens modelocked Ti:Sapphire oscillator regeneratively amplified by a flashlamp pumped Cr:LiSAF amplifier, producing 110 fs (FWHM) laser pulses with a Gaussian temporal profile at 845 nm. The second laser is the unseeded CrLiSAF regener-

ative amplifier, which produces long (60 ns) Q-switched pulses, at 845 nm, from which square 10 ns pulses are sliced using an extra-cavity Pockels cell as an electro-optical pulse cutter. The third laser is a flashlamp pumped Q-switched Nd:YAG laser that produced 15ns (FWHM) Gaussian-shaped laser pulses at 1064 nm. The laser parameters are listed in **Table 1**.

Each setup was identical, only differing in the laser source: The laser beam is expanded using a 4:1 telescope and filtered by an iris. It is then focused to a 100μm diameter spot onto the target using a fused silica plano-convex lens with a 20 cm focal length. After initial positioning, the focus spot was not moved during the ablation. The holes are drilled parallel to the long axis of thin polished glass plates.

Table 1 Laser parameters

Laser	Wavelength λ (nm)	Pulse Duration t_p Pulse Energy, E_p	Repetition Rate, R (Hz)	Focal Spot Diameter, D (μm)	Laser Fluence, F_p (J/cm^2)	Focal Intensity, I_p (W/cm^2)
Ti:Saph/ Cr:LiSAF	845	110 fs (FWHM) 1.5 mJ	5	100 (FW1/e^{2}M)	19.1	1.74×10^{14}
Cr:LiSAF	845	10 ns (FWHM) 4.0 mJ	5	100 (FW1/e^{2}M)	51.0	5.10×10^{9}
Nd:YAG	1064	15 ns (FWHM) 2.2 mJ	10	100 (FW1/e^{2}M)	28.0	1.87×10^{9}

3.2 Results

Optical microscope images of the holes produced by 10^4 laser pulses in soda-lime silicate glass and PbO lead-silicate glass are shown in **Figure 2** and **3**.

The overall penetration depth is significantly greater for PbO lead-silicate than for soda-lime silicate glass in the three different ablation scenarios due to a higher Z resulting in a higher electron density. In addition, there is a drastic difference in hole depth and width between **Figure 2b** and **Figure 2c**, which illustrates the variations in ablation mechanism and hole morphology obtained in the nanosecond regime at 845 nm and 1064 nm. Furthermore, in both materials, the femtosecond ablation is more energetically efficient as greater penetration depth are obtained with a smaller energy per pulse.

The same experiments were now made in the femtosecond regime at fluences sufficient to ionize the air. The fluence of the laser was increased by reducing the beam spot size from 100 μm to 75 μm. We compare the femtosecond laser ablation of the two silicate glasses below and above the air ionization threshold in **Figure 4.** Below air ionization threshold, the abla-

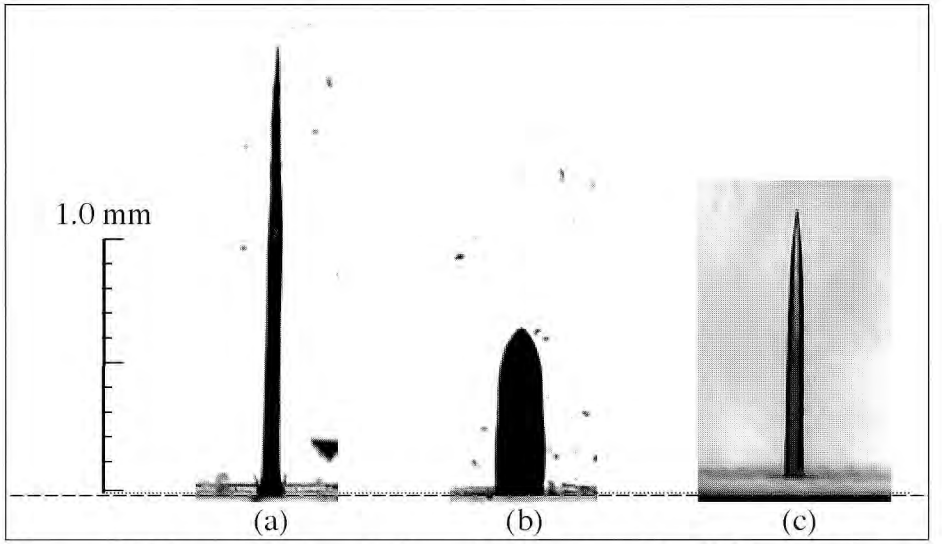

Figure 2 Hole profiles in soda-lime glass produced by 104 laser pulses
(**a**) λ = 845 nm, t_p = 110 fs, E_p = 1.5 mJ, $I_p = 1.74\times10^{14}$ W/cm^2, Fp = 19.1 J/cm^2
(**b**) λ = 845 nm, t_p = 10 ns, E_p = 4.0 mJ, $I_p = 5.10\times10^{9}$ W/cm^2, Fp =51.0 J/cm^2
(**c**) λ = 1064 nm, t_p = 15 ns, E_p = 2.2 mJ, $I_p = 1.87\times10^{9}$ W/cm^2, Fp =28.0 J/cm^2

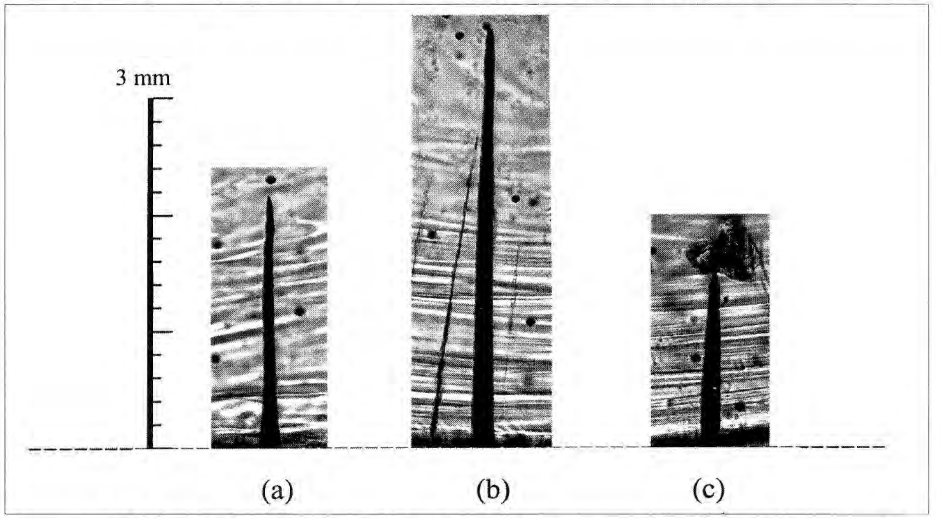

Figure 3 Hole profiles in 45% mol. lead silicate glass produced by 10^4 laser pulses
(**a**) λ = 845 nm, t_p = 110 fs, E_p = 1.5 mJ, $I_p = 1.74\times10^{14}$ W/cm^2, F_p = 19.1 J/cm^2
(**b**) λ = 845 nm, t_p = 10 ns, E_p = 4.0 mJ, $I_p = 5.10\times10^{9}$ W/cm^2, F_p =51.0 J/cm^2
(**c**) λ = 1064 nm, t_p = 15 ns, E_p = 2.2 mJ, $I_p = 1.87\times109$ W/cm^2, F_p =28.0 J/cm^2

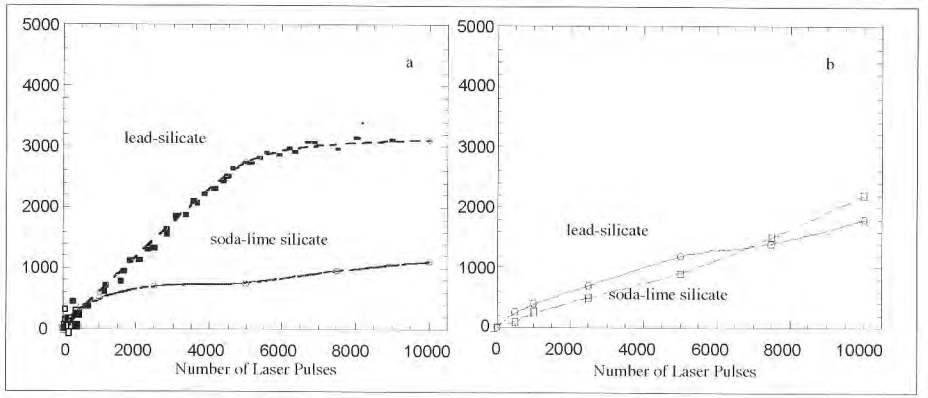

Figure 4 Laser penetration depth (μm) vs. number of incident laser pulses (t_p = 110 fs, l = 845 nm, E_p = 1.5 mJ) given:
(**a**) $I_p = 3.08 \times 10^{14}$ W/cm^2, F_p = 33.9 J/cm, and d = 75 μm (FW1/e^{2}M)
(**b**) $I_p = 1.74 \times 10^{14}$ W/cm^2, F_p = 19.1 J/cm^2, and d = 100 $_m$m (FW1/e^{2}M)

tion rate remained constant over the tested range at ~0.2 μm/pulse for both glasses. Above threshold, the ablation rate rises up to ~0.5 μm/pulse and rapidly reduces down to ~0.05 μm/pulse (at ~1000 shots for soda-lime and ~5000 shots for PbO silicate glass). It can be seen that there is a striking increase in the ablation-rate for the PbO glass at higher intensities.

A number of explanations are possible. First, we know that the influence of the air ionization makes a change to the ablation rate.[8] However, the interaction physics with the higher Z glass could also be playing a role, and one cannot exclude the possible differences in material properties. Optical probe images, taken during the laser material interaction above ionization threshold, revealed that after a certain depth is achieved, light starts to form a thin (~10 μm) hot filament confined inside the hole (**Figure 5**).

High-intensity ultrashort laser pulses propagating in air have been observed to self-channel into light filaments exceeding the Raleigh length.[9] It is believed that a similar effect occurs because of evaporated material that remains temporarily confined in the hole, thus increasing the nonlinear index of refraction of the atmosphere. More evidence of this effect is present in **Figure 6** where very sharp holes pointing in slightly different directions are shown at the tip of the hole both in lead silicate glass and As_2S_3, a chalcogenide glass. These pins could be attributed to ablation due to self-channeled single shots. Note that the individual pins or filaments in the material are uniformly ~ 100 mm long. In addition, it is important to note that the rollover in the ablation rate described above occurred earlier for PbO lead silicate than for soda-lime silicate. The pres-

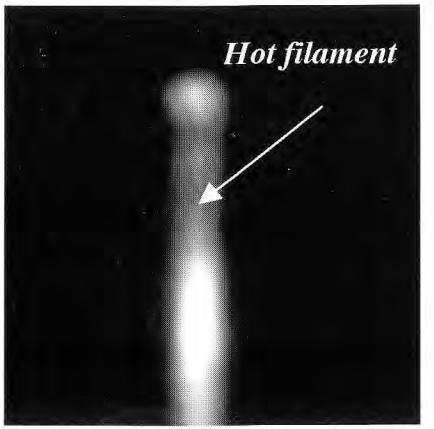

Figure 5 Hot filament inside an ablated hole in lead silicate glass.

ence of high Z elements (PbO) or particles of highly non linear material (As_2S_3) in the hole atmosphere can account for a higher nonlinear index of refraction, thus lowering the intensity threshold for self-focusing.

4. Grating fabrication in thin films of chalcogenide glass

Femtosecond lasers appear to be a promising tool for the micro-structuring of optical materials. It was demonstrated that unamplified femtosecond lasers could produce optical breakdown and structural change in bulk transparent materials using tightly focused pulses of just 5 nJ[10].

4.1 Grating fabrication

Using an extended cavity unamplified Kerr-lens modelocked Ti:Sapphire laser, relief and volume gratings with a 20 μm period were fabricated on a 1.66 μm thick, As_2S_3 thin film. The laser emission has a spectral bandwidth of approximately 40 nm (FWHM) centered at 800 nm and a repeti-

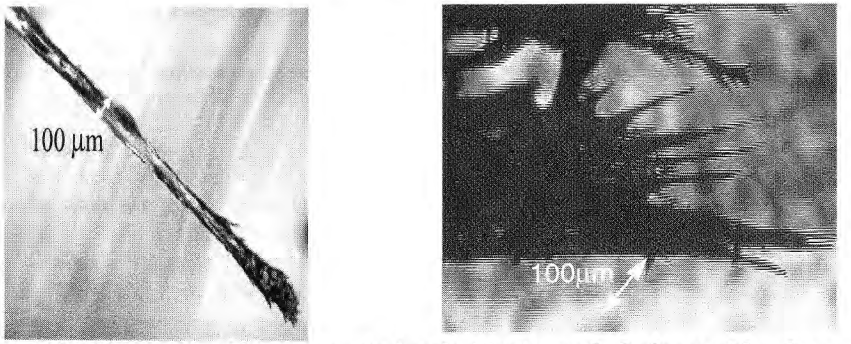

Figure 6 Evidence of self-focusing in lead silicate and chalcogenide glass.

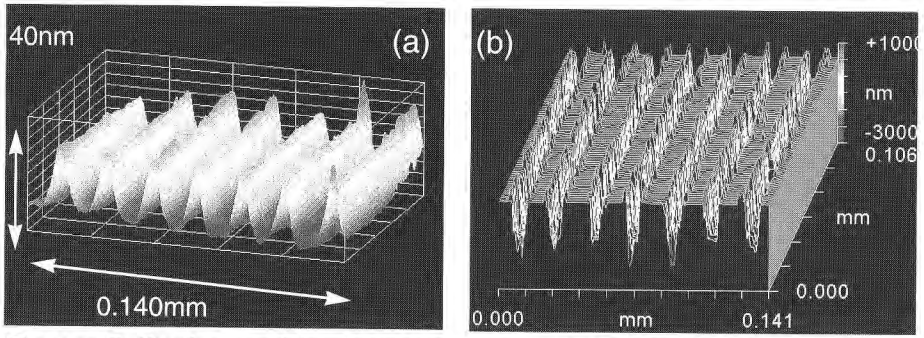

Figure 7 Surface profile of (**a**) the phase and (**b**) relief grating on the As_2S_3 film produced with sub-50 fs laser pulses from the extended cavity Ti:Sapphire oscillator.

tion rate of 27 MHz. An interferometric autocorrelation measured sub-50 fs pulse duration. The system has an average output power of 0.55 W and produces energies up to 20 nJ per pulse. The output of the laser was focused by a 15x, 0.28NA reflective objective onto a target attached to a 3D motorized translation system.

The sample was processed in two regimes: Firstly, the intensity was kept below the ablation threshold, generating a volume grating resulting from photoexpansion and an induced index change, as observed through an interferometric microscope. In the second regime, intensities above the ablation threshold produced a relief grating with grooves of ~2 μm depth (**Figure 7**).

4.2 Waveguide fabrication

Previous studies have linked bulk glass structural and optical property changes (photosensitivity) through Raman spectroscopy, showing thatnonlinear absorption-induced index changes were linked to local bonding changes in As_2S_3[11]. Following this approach, waveguides over 1 cm in length and ~10 mm in diameter were fabricated in As_2S_3 thin films by direct transverse writing using the same 27 MHZ, 20 nJ, 100 fs, Ti:Sapphire laser (**Figure 8**).

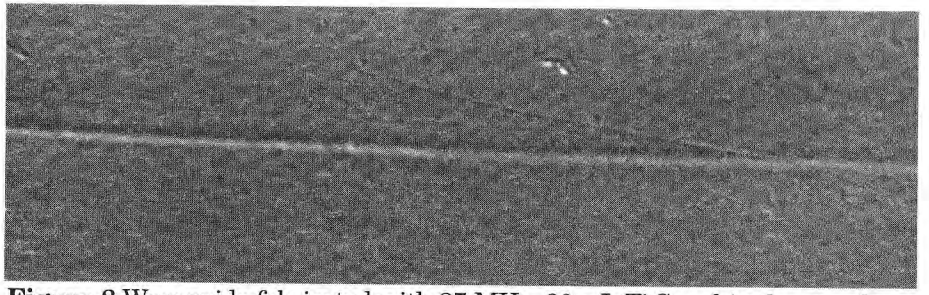

Figure 8 Waveguide fabricated with 27 MHz, 20 nJ Ti:Sapphire laser pulses

Further studies are underway including the measurement of the refractive index change by the refracted near-field technique. In addition, waveguide Raman spectroscopic measurements in the film will be compared to the previous results in bulk to confirm the molecular bond changes that give rise to the change of refractive index.

This technique has already established its ability to create complex waveguide structures in optical materials. For instance, directional couplers and 3D-waveguides were fabricated using a nanojoule laser in borosilicate glass[12] and soda-lime glass. With a reduced complexity of operation and an increased cost-effectiveness, nonlinear material processing with near-IR femtosecond pulses will be of interest to optical communication systems manufacturers for miniaturization and integration of photonic devices.

5. Conclusions

This study illustrates the ability of femtosecond material micro-processing to produce very fine surface structures and its versatility both in the type of processing and the type of materials to be processed. Comparison between the femtosecond and nanosecond regimes has shown that finer, more energy-effective and more material-independent structuring could be obtained with femtosecond pulses.

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