

OPTICALLY TRANSFORMING GLASS: AN INTRODUCTION

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ABSTRACT

Laser processing of glass is used for a number of purposes including cutting, marking, and direct holographic exposure of bulk and waveguide glasses. Of interest to many of us at this workshop is direct writing of waveguides, components and structures in various glassy materials in both bulk and waveguide form. All involve some form of energy deposition to affect some change in the material, ranging from refractive index change through polarisability or density changes, to ablation and other damage mechanisms initiated above the threshold for numerous phenomena in glass, including photo ionisation, melting and oxygen release. A brief overview introducing the workshop and its motivations will be presented.

Laser processing of glass is used for a number of purposes including cutting, marking, and direct holographic exposure of bulk and waveguide glasses. Of interest to many of us at this workshop is direct writing of waveguides, components and structures in various glassy materials in both bulk and waveguide form. All involve some form of energy deposition to affect some change in the material, ranging from refractive index change through polarisability or density changes, to ablation and other damage mechanisms initiated above the threshold for numerous phenomena in glass, including photo ionisation, melting and oxygen release. There has been decades of work understanding and quantifying radiation effects, including gamma rays, nuclear particles, and UV light, on glass [McClelland & Donoghue 1953; Weeks 1956; Gelardi & Agnello 2000 and refs therein]. These involve excitation within the band edge of silica, often well below the UV region. This has been carried out mainly to understand the impact of ionisation processes on oxides generally including those used in semiconductors and hence the longevity and ultimate size of these devices. Of particular note, was the observation and study of glass densification and dilation using UV light below the damage threshold of the glass [Primak 1953; Primak 1958; Primak & Kampwirth 1968; Fiori & Devine 1986]. The relatively long timescales meant behaviour analogous to thermal quenching is involved [Wootten et al. 2001]. The impact of ionisation continues to be investigated today, for the semiconductor industry and for potential exploitation as means of either resisting or detecting radiation in a nuclear environment, civil or military.

The “newest” kid on the block in current glass engineering (at least from a device perspective) has become the two or more multiphoton pathway required when using UV light to access the band edge glass in order to achieve essentially densification and a refractive index change. Historically in studying the effect of ionising radiation on glass, the wavelength of choice has typically been 193nm, which requires a two photon excitation to access sufficiently deep into the band edge. The nature of this two photon process has raised some controversy in terms of the contributions arising from two photon excitation via a virtual transition or an excited state intermediary. However, the behaviour of radiation loaded glass is consistent with an analogous

thermal quenching of the system, where the cooling rate determines the structure and therefore refractive index achieved [Wootten et al. 2001]. It is in principle possible to select between densification and rarefaction of the glass by controlling the intensity, repetition rates and even the background temperature at which exposure is taking place. Though the details are not yet well known, two photon excitation is now used to write Bragg gratings into pure silica core fibres, for example [Albert et al. 2002; Groothoff et al. 2003], and two of the presentations will review both the writing process and the properties of such gratings. Longer UV wavelength excitation at 248nm has also been used to study radiation induced densification of glass, as has higher photon absorption above 300nm, but in these cases the excitation by two photon absorption is increasingly ineffective with increasing wavelength and usually three photon absorption is required. As a general rule the deeper in the UV one goes the better the performance, although in the one photon regime some of the practical challenges involved with dealing with wavelengths below 180nm often negate this. For example, direct grating written at 157nm in pure silica photonic crystal fibres, into which two photon 193nm excitation has produced gratings, has not been terribly successful. This may in part be due to the additional requirements of removing air from the air holes which, in addition to scattering can attenuate the 157nm before reaching the central guiding region. Other solutions used to reduce scattering by placing organic liquids in the holes [Sørensen et al. 2006] are problematic as very few liquids have low absorption at 157nm. At the longer UV wavelengths, the problem then is one of controlling the necessary higher order process without generating the thermal build up that can lead to damage, such as has been utilised to produce either single or few shot type II damage gratings [Askins et al. 1992; Hill et al. 1995]. Although feasible the quality of the gratings are generally poor and the background scattering losses high – the index change localisation is diffuse and uncontrolled, although the application of stress appears to help [Hill et al. 1995]. This thermal build-up occurs because the local phonon decoupling rate is much faster than the energy deposition time (the time taken to excite the electronic degrees of freedom as opposed to the various vibrational modes of the local system associated with phonon excitation) involved with typically nanosecond, or in some cases, picosecond pulses. That is the associated relaxation processes as energy is decoupled away from the excitation source are often on a timescale ranging from femtoseconds to nanoseconds in the short term relevant to the engineering process at hand (although relaxations within a glass system can in principle well beyond this, sometimes well beyond the practical consideration of the task at hand). Further, the whole process is complicated by additional mechanisms when electronic transfer processes are also considered. The separation of both electronic transport and thermal relaxations is probably unrealistic in practice. At very high intensities electrons can be ionised and be highly energetic and their subsequent transport can be independent of the excitation timescales so even between two photon and multiphoton excitation processes, there may be very little distinction at similarly high intensities. In metals this behaviour is often ballistic and their transport over scales much larger than the optical depth [Tas & Maris 1994].

In addition to both thermal and electronic relaxation processes, there are associated changes in the local stresses and strains created between the excited region and the surrounding material. Indeed, it is from such changes that certain authors have inferred a dependency on the role of the polarisation state of the laser exposing the samples and the induced birefringence within the affected glass change [Smith et al. 2001]. Conversely applying a stress or strain during irradiation will similarly affect

the induced changes – this forms the basis for UV-induced birefringence within optical fibres loaded with hydrogen and exposed to single photon UV excitation [Canning et al. 2005]. The role of polarisation has even more interesting effects and one of the presenters will talk of how nano-patterning is possible by triggering self organisation phenomena imposed by laser polarisation and subsequent anisotropic scattering onto the generated electron-ion plasma, amongst other things. This work extends into three dimensions the self-interference patterns observed previously on surfaces during ablation studies and suggests that it can be exploited to develop novel nanotechnology. One presentation also discusses how numerical simulations are making headways in understanding some of the details of the plasmas generated by such intense light.

Thus it is now clear why, with the advent of high quality femtosecond lasers, interest has increased tremendously in ultrafast material processing generally. These lasers distinguish themselves in their ability to deposit the required total photon energy on a timescale commensurate to or faster than all these relaxation and diffusion times. At the very high intensity regime, within the focal volume of the lens used, both nonlinear field ionisation, and avalanche ionisation, where an ionised electron has sufficient energy to go and ionise another electron and potentially triggering a cascade of such processes, are possible. The pulse duration is much shorter than the lattice heating time and thermalisation between the excited electrons and the lattice does not occur. Indeed, by controlling both the intensity and pulse width it may be possible to control access to various ionisation, transport and relaxation processes – they can, in principle, at sufficiently low repetition rates be completely separated from the excitation process. Selective access may at least therefore be of fundamental scientific interest in studying individual and groups of relaxations, something which is only becoming possible with increasing advances in laser technology. For example, in the low intensity regime where we avoid all multiphoton effects by using a UV femtosecond laser we can directly compare processing against existing long pulse or CW UV lasers. This allows an unambiguous study of the role of the pulse duration on affecting index change through well understood conventional means such as through polarisability changes of oxygen deficient centres in germanosilicate glasses. To this end, in collaboration with Southampton University we compared 266nm femtosecond excitation of germanosilicate optical fibres with CW 244nm excitation [Canagasabey et al. 2006]. Importantly, we found no evidence of any distinction between the two, neither in the growth in index change or the subsequent thermal annealing to stabilise that index change, despite the difference in timescale. Thus it is possible to conclude that the excitation path occurs on a very short timescale and is largely independent of subsequent local relaxations. Given the importance of this approach to affecting low loss, extremely reproducible index change within the Bragg grating industry, for example, and the very high level of sophistication possible with long spatial and temporal coherence length of existing CW or long pulse UV lasers, it is difficult to see femtosecond lasers genuinely competing in this regime. On the other hand, as a few presentations in this workshop will illustrate, where low loss and very complex grating quality are not an issue, then femtosecond lasers operating in the high intensity regime can fabricate quickly gratings for specific applications, including high power fibre lasers.

Femtosecond processing also has the added advantage that in principle it appears it can bypass any intermediary transient species associated with longer pulse excitations

or electronic excitation after ionisation provided such species require a longer time of formation than the pulse duration but shorter than the exposure duration determined by the repetition rate. If correct, then the nature of the excitation may be substantially different fundamentally beyond the rapid excitation to bypass the longer duration relaxation process associated with glass where energy has been deposited. However, given that melting and significant structural change have been observed in these glasses, much of the relaxation phenomena after excitation have some analogy to the quenching interpretation of the two 193nm photon long pulse excitation induced relaxations although highly localised since there is no thermalisation of the glass network. A practical difference that is well understood is the spatial localisation of the phenomena because the two or higher exponent process can allow very tight localisation of the light, below the diffraction limit [Tanaka et al. 2002]. It is worth mentioning that such localisation using multiphoton excitation in combination with a nonlinear process is a general means of circumventing the diffraction limit and has been applied to fluorescence microscopy [Hell S.W., 2004].

In combination with the spatial selectivity offered by even higher order photon absorption pathways accessible to longer wavelengths, the thermal build-up and indeed runaway in some cases, along with other diffusive phenomena can be contained and highly localised using femtosecond pulsed lasers. Thus a new regime for exploring, for example, what has been labelled “type II” in the fibre gratings literature, is accessible. Given the explosion of work in this area and the controversy regarding the underlying mechanisms, it is therefore only natural that the bulk of the presentations of this workshop focus on this area. Just how far can these lasers be pushed? In part this workshop seeks to address this question and some of the presentations will describe numerous ways of using these lasers to make practical components, including gratings for high power fibre lasers, as well as to move towards better control of both the induced amplitude and corresponding phase.

At the other end of the wavelength scale, another interesting “revival” is occurring. Again associated very much with technological developments and in particular the development of very high quality x-ray sources, glass processing directly at very short wavelengths is increasingly sophisticated and practically possible. Specifically, new state-of-the-art synchrotron sources are being built in several places around the world, including Paris, France and in Melbourne, Australia. In addition to raw x-rays, these sources also generate many wavelengths across the spectrum including high coherence UV wavelengths of interest to lithography. The recent rise in interest in glass processing using the output from these synchrotron sources forms the basis of the special session in the workshop dedicated to the current work in this area. It can significantly extend the field of radiation studies of glass as well as possibly opening up alternative lithography approaches to numerous problems in the future. Such are the remarkable advances in technology, in particular the power and quality of the beams produced, that it is conceivable in the not too distant future that practical x-ray sources may exist, some potentially generated by the very plasmas femtosecond lasers can produce [Rousse et al. 2004]. Such is the progress in technology that many researchers in this area feel applications such as fibre Bragg grating writing with these sources is within reach today.

It is clear from the brief overview above that technology remains a key driver of the possibilities being envisaged, both scientific and engineering-wise. Therefore, there is

a presentation giving an overview of developing femtosecond technology and what may be expected in the next generation of lasers for material processing generally. Since these lasers are applicable to a whole range of materials, not just glass, a presentation is also given on how they are being applied to the engineering of complex structures in 3-dimensions within polymer materials. It is of particular value to understand just how generic some of these processes are regardless of the material system and the purpose of the workshop is to offer the opportunity to examine both similarities and differences between materials. To this end it is also not unreasonable to suppose that developments in attosecond lasers will take this degree of selectivity or “resolution”, localisation and refinement still further.

Developments in enabling technologies are clearly a critical feature of progress in the application of laser processing. For materials processing on micro and nano scales, work towards a new generation of measurement tools and characterisation approaches that allow more refined and detailed analysis than was previously possible is equally important. To describe some of the tools available for characterising properties such as index and density, various techniques will be outlined in one presentation, including those based on highly localised spatial characterisation which is becoming increasingly important in the verification and demonstration of complex structures. To highlight other concerns distinct from the study of the bulk of the material alone, another presentation discusses detailed research on surface interactions, focussing on UV interactions with silica, including contaminants that can affect the changes one wishes to attain. In addition to distinct interaction that can arise as result of unique surface defects and their often higher concentrations, high quality interfaces and ultra cleanliness increasingly play a critical role in determining the reproducibility of much the applied technology. The sensitivity of a higher order exponent process to any surface variations or scatterers also raises some interesting questions.

Finally, it is worth pointing out that despite the breadth and depth being covered by this workshop, the field remains incredibly rich with many areas unlikely to be fairly represented here. For example, straightforward applications of much of the above can similarly enable technologies in different materials other than silica and polymer, such as other oxide glasses, chalcogenides and fluorides. Many of these have their own peculiar challenges. In conclusion, the workshop brings together a selection of some of the world’s best experts in the specialised topic areas described above. It also brings together young scientists, both students and early career researchers, who will benefit from the interdisciplinary nature of the presentations – the field of material processing spans both fundamental chemistry and physics through to all aspects of device and technology engineering. It is therefore apt that the last presentation should take us into another exciting area of research, “nanooptics”, and discusses how multiphoton processes can play a role in these devices, something a little different again.

Albert J., Fokine M., Margulis W., (2002) *Opt. Lett.*, 27 (10), 809-811

Askins C.G., Tsai -E.T., Williams G.M., Putnam M.A., Bashkansky M., Friebele E.J., (1992), *Opt. Lett.*, 17, 833-835

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Canning J., Deyerl H.J., Sørensen H.R., Kristensen M., (2005) *J. of Appl. Phys.* **97**,

053104

- Dragomir A., McInerney J.G., Nikogosyan D.N., (2002) *Appl. Opt.*, 41 (21), 4365
- Dragomir A., Nikogosyan D.N., Zagorulko K.A., Kryukov P.G., Dianov E.M., (2003) *Opt. Lett.*, 28 (22), 2171
- Fiori C., Devine R., (1986) *Phys. Rev. B* 33, 2972
- Gelardi F.M., Agnello S., (2000) in Defects in SiO₂ and related Dielectrics: Science and Technology, (Ed. G. Pacchioni, L. Skuja, and D.L. Griscom), Nato Science Series, 11 Mathematics, Physics and Chemistry, Vol. 2, Kluwer Academic Publishers
- Grothoff N., Canning J., Lyytikainen K., Zagari J., *Opt. Lett.*, **28**, (4), pp. 233-235, (2003)
- Hell S., (2004) *Phys. Lett. A* 326, 140-145
- Hill P., Atkins G.R., Canning J., Cox G., Sceats M.G., (1995) *Appl. Opt.*, **33**, (33), 7689-7694
- McClelland J.D., Donoghue J.J., (1953) *J. Appl. Phys.* 24, 963
- Mihailov S.J., Smelser C.W., Lu P., Walker R.B., Grobncic D., Ding H., Henderson G., Unruh J., (2003a) *Opt. Lett.*, 28 (12), 995-997
- Mihailov S.J., Smelser C.W., Lu P., Walker R.B., Grobncic D., Ding H., Unruh J., (2003b) *J. Lightwave Technol.* 22, 94
- Primak W., (1953) *Phys. Rev.* 92, 1064-1065
- Primak W., (1958) *Phys. Rev.* 110, 1240-1254
- Primak W., Kampwirth R., (1968) *J. of Appl. Phys.* 39, (12), 5651-5658
- Rousse, A., Phuoc K.T., Shah R., Pukhov A., Lefebvre E., Malka V., Kiselev S., Burgy F., Rousseau J.P., Umstadter D., Hulin D., (2004) *Phys. Rev. Lett.*, 93 135005
- Smith C.N., Borelli N.F., Price J.J., Allen D.C., (2001) *Appl. Phys. Lett.* **78**, 2452
- Tanaka T., Sun H.-B., Kawata S., (2002) *Appl. Phys. Lett.*, 80 (2), 312-314
- Tas G., Maris H.J., (1994) *Phys. Rev. B*. 49, 15046-15054
- Weeks R.A., (1956) *J. Appl. Phys.* 27, 1376
- Wootton A., Thomas B., Harrowell P., (2001) *J. Chem. Phys.* 115 (7), 3336