

# Raman analysis of laser-processed glass materials

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Laser processing provides a fast, non-contact and flexible method of modifying and patterning materials, from glasses to metals. Micro-machining, thin layers ablation, two-photon polymerization are just a few examples of what has already been demonstrated. Glasses, or more generally, optical materials, may react to laser irradiation by changing their refractive index. This effect has been successfully used to create three-dimensional structures inside bulk glass (waveguides, optical memories, volume Bragg gratings, etc).

## Photo-structural changes induced by laser irradiation

Laser processing often results in photo-structural changes, whether during ablation or the more subtle modification of the refractive index. Raman spectroscopy has proven to be very useful to understand the photo-structural changes underlying the processing.

### 1) In Arsenic sulfide ( $As_2S_3$ )

Arsenic sulfide belongs to the chalcogenide glass family, which exhibits several interesting properties that can be exploited for the fabrication of photonic devices. In particular, their excellent infrared transparency, large nonlinear refractive indices, and low phonon energies make them good candidates for use in the fabrication of all-optical switches and as integrated optical elements.

The Raman spectrum of vitreous  $As_2S_3$  is dominated by the strong band at  $\sim 345\text{ cm}^{-1}$  attributed to the symmetric stretching vibrational mode of  $AsS_{3/2}$  pyramids. Besides this strong band, there are additional features (shoulders) at approximately  $310$  and  $380\text{ cm}^{-1}$ , which are assigned to the asymmetric stretching modes of  $AsS_{3/2}$  pyramids and  $As-S-As$  bridges, respectively. The presence of sulphur in excess in the thin film form is indicated by the weak band at  $485-495\text{ cm}^{-1}$  associated with the  $S-S$  stretching vibration in  $S_8$  rings. Weak bands situated at  $188\text{ cm}^{-1}$  and  $235\text{ cm}^{-1}$  can be attributed to the bending modes of  $AsS_{3/2}$  pyramids,  $S_8$  and  $As_4S_4$  molecules. Ideally, the spectrum should only consist of the strong band at  $345\text{ cm}^{-1}$ .

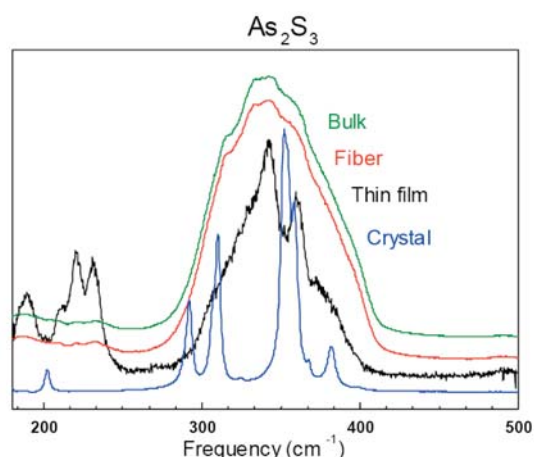


Figure 1. Raman spectrum of  $As_2S_3$  in bulk, fiber, thin film and crystal form.

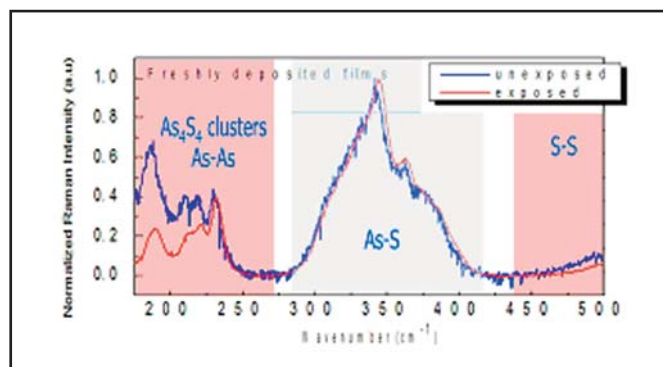
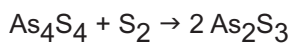


Figure 2. Comparison between the Raman spectrum of arsenic trisulfide unexposed (blue curve) and exposed to the laser (red curve).

The presence of the additional structures mentioned above is due to the formation of “wrong bonds” in the glass network. This is particularly visible in the thin film form (Figure 1), where  $As_4S_4$  molecular clusters and As-As homopolar bonds are created during the deposition process.

After irradiation, the peaks at the low wavenumbers, corresponding to the presence of  $As_4S_4$  molecules, show a significant decrease in intensity (Figure 2). This is interpreted as a decrease in the content of  $As_4S_4$ , due to the photosynthetic reaction whereby the original stoichiometry is recreated, partially reforming the  $As_2S_3$  network according to:



Concurrently, the relative intensity of the peak at  $235\text{ cm}^{-1}$ , linked to the presence of As-As homopolar bonds, exhibits a relative increase, due to the photolytic reaction whereby As-S heteropolar bonds decompose to yield “wrong” homopolar bonds, according to:



## 2) In Silicon Oxide ( $SiO_2$ )

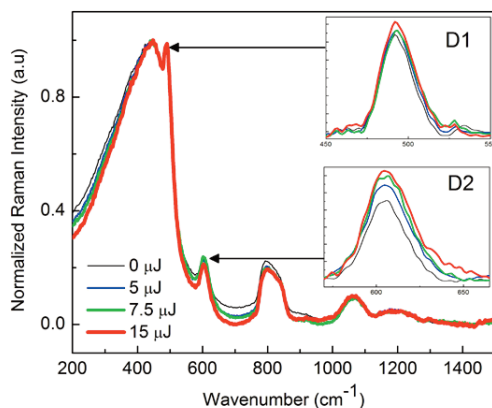


Figure 3. Raman spectra of pristine and fs IR laser-irradiated fused silica with increasing laser pulse energies. The insets are magnified images of the D1 and D2 lines at  $490\text{ cm}^{-1}$  and  $606\text{ cm}^{-1}$ , respectively.

Raman spectroscopy has proven an efficient method of characterizing structural modification in fused silica.

The main feature of the spectrum of fused silica is the broad band centered at around  $440\text{ cm}^{-1}$ , attributed to the Si-O-Si bond rocking and bending in  $SiO_4$  tetrahedra. The two smaller bands at  $490\text{ cm}^{-1}$  (D1) and  $606\text{ cm}^{-1}$  (D2) have been attributed to three- and four-member siloxane rings, respectively, in the silica network. The comparison of these spectra between pristine and irradiated samples (Figure 3) reveals two principle trends as the pulse energy is increased:

- 1) the amplitude of both defect lines D1 and D2 increases
- 2) the width of the main band at  $440\text{ cm}^{-1}$  decreases.

The increased amplitude of the D1 and D2 defect peaks is attributed to the change in ring statistics where six-fold rings transform to three-fold and four-fold rings upon laser irradiation. The narrowing of the main  $440\text{ cm}^{-1}$  band with increasing irradiation energy, has also been reported in the case of  $\beta$  irradiation. The frequency of this band relates to the Si-O-Si angle in the glass network, and its width reflects the distribution of the Si-O-Si angle. The narrowing of the  $440\text{ cm}^{-1}$  band can therefore be explained by photoinduced ruptures of the strained Si-O-Si bridging bonds which are more likely to break than unstrained bonds.

## 3D waveguide writing in bulk glass

A femtosecond Ti:Sapphire laser is focused inside a bulk glass sample. The sample is moved using a motorized stage and the refractive index is modified at the laser focus along the path followed by the stage (Figure 4). If the refractive index change is positive, this creates a waveguide (Figure 4) much like an optical fiber embedded inside the glass sample. This lays the ground for producing 3-D optical circuits.

A. Zoubir et al., « Direct femtosecond laser writing of waveguides in  $As_2S_3$  thin films », *OPTICS LETTERS* / Vol.29, No. 7 / April 1, 2004  
 A. Zoubir, et al., « Laser-induced defects in fused silica by femtosecond IR irradiation », *PHYSICAL REVIEW B* 73, 224117 (2006)

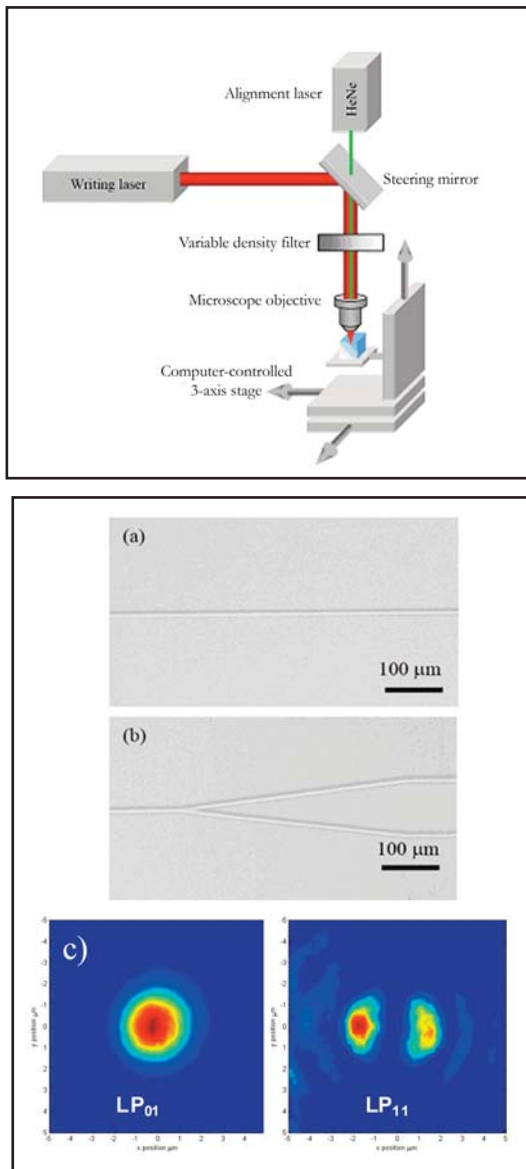


Figure 4 - Optical microscope images of (a) a single channel waveguide, (b) a Y-coupler, and (c) near-field intensity profile of the LP01 and LP11 modes in a single-channel waveguide.