Optical and Photonic Glasses

Lecture 28:
Photochromic and Photosensitive Glasses

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Photochromic and photosensitive glasses

Photochromic glasses are those which, upon exposure to solar radiation, or any other type of radiation with a UV component, darken in a reversible fashion, undergoing bleaching as the exposure is stopped. *Reversibility* is a key factor in this case.

Such glasses contain atoms or molecules which may occur in two states with different electronic configurations and different light absorption coefficients.

Photochromic glasses are normally used in ophthalmic lenses, or in building or automobile windows (although they can be replaced by *electrochromic* glasses in the latter two applications).

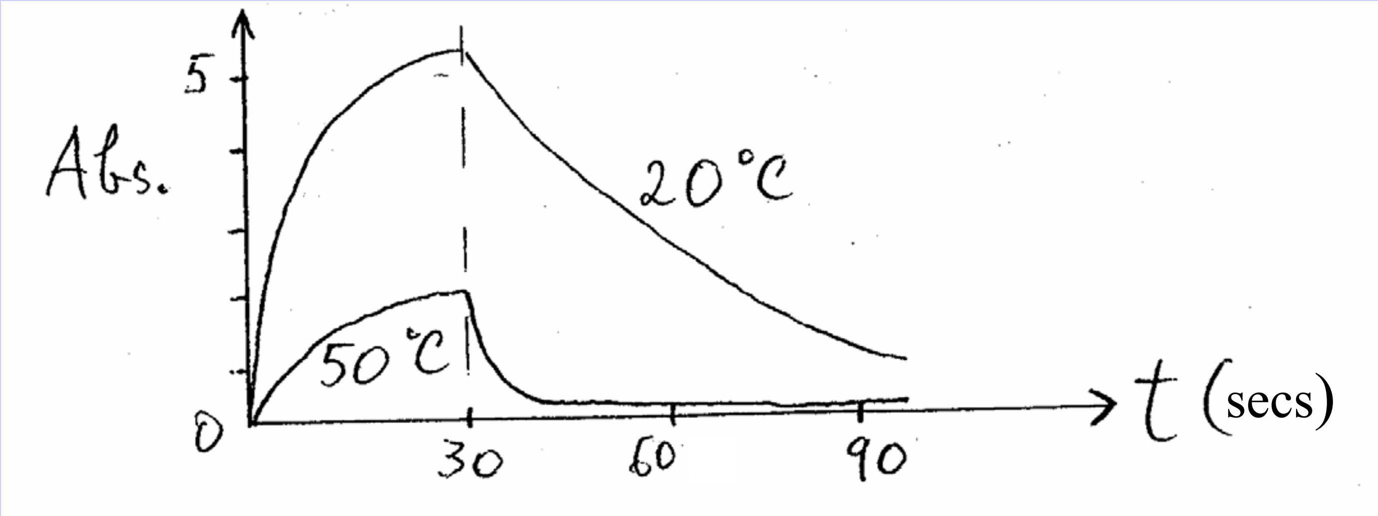
Commercial photochromic glasses are usually alkali borosilicates which also contain a small concentration of AgCl (~ 0.2 – 0.7 weight %). In addition, some AgBr or AgI may also be present. A heat treatment after melting and casting causes the formation of AgCl nanocrystals ~ 10 nm in diameter.

The reversible photodarkening phenomenon appears to be the result of a precipitation of minute grains of Ag^o metal (without release of the gaseous halogen), which absorb visible light:

$$2\ AgCl \xrightarrow{h\nu} 2\ Ag^o + Cl_2\ (g)$$

The particular range of wavelengths which cause darkening of the glass depend primarily on the halide present. AgCl is sensitive to the UV and violet, whereas the addition of Br or I shifts the sensitivity to longer wavelengths.

It has been found the rate of darkening is practically insensitive to the temperature, but the bleaching rate increases with temperature:



Photosensitive glasses

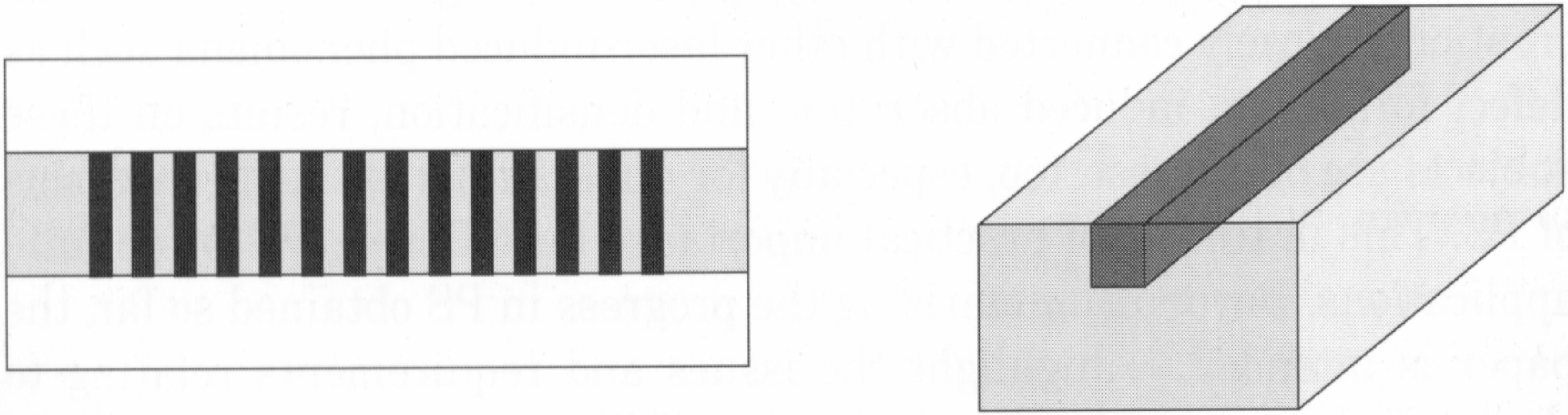
Photosensitive (PS) glasses are those in which permanent refractive index changes, Δn, are induced by laser light exposure. This is of great importance for the direct writing of micro and nanostructures, such as gratings and waveguides, in glasses for optical and photonic devices.

Fabrication techniques

While gratings require a periodic refractive index modulation, waveguides consist of a constant Δn in one or two dimensions (for channel or planar waveguides, respectively).

Waveguide writing is very attractive for the fabrication of channel waveguides in compact optical devices, compared with photolithography and reactive ion etching.

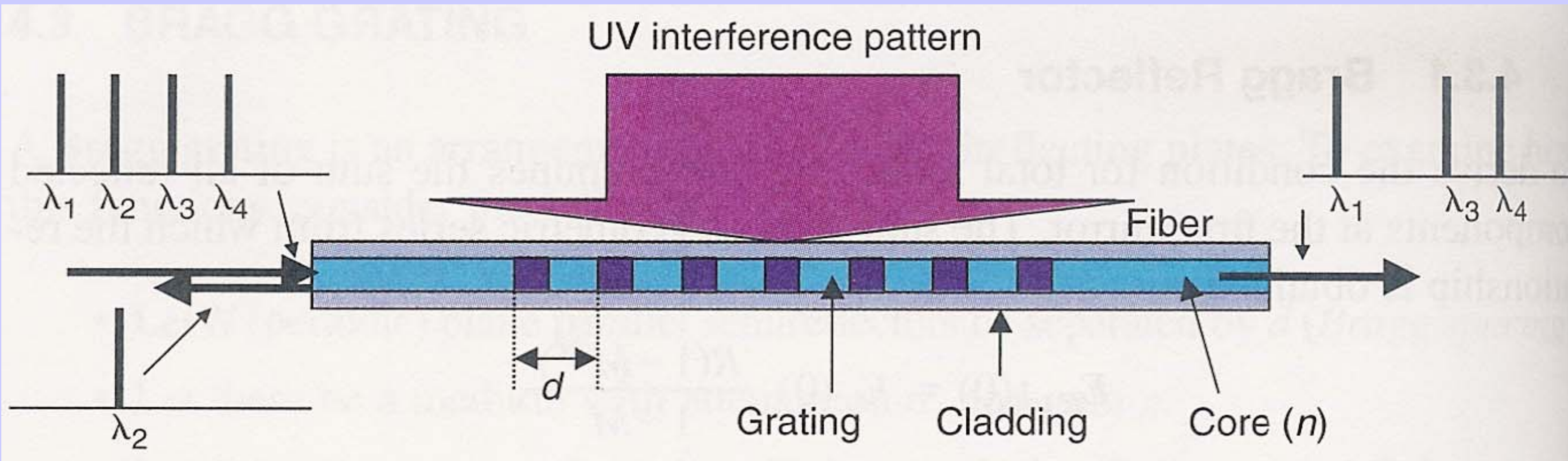
The combination of the two structures is also attractive: first writing a waveguide and then imprinting a grating on this waveguide.



Schematic illustration of fiber Bragg grating (left) and channel waveguide (right).

(Adapted from: H.E. Heidepriem in, *Glass and the photonics revolution*, Glass Sci. Technol., 2002)

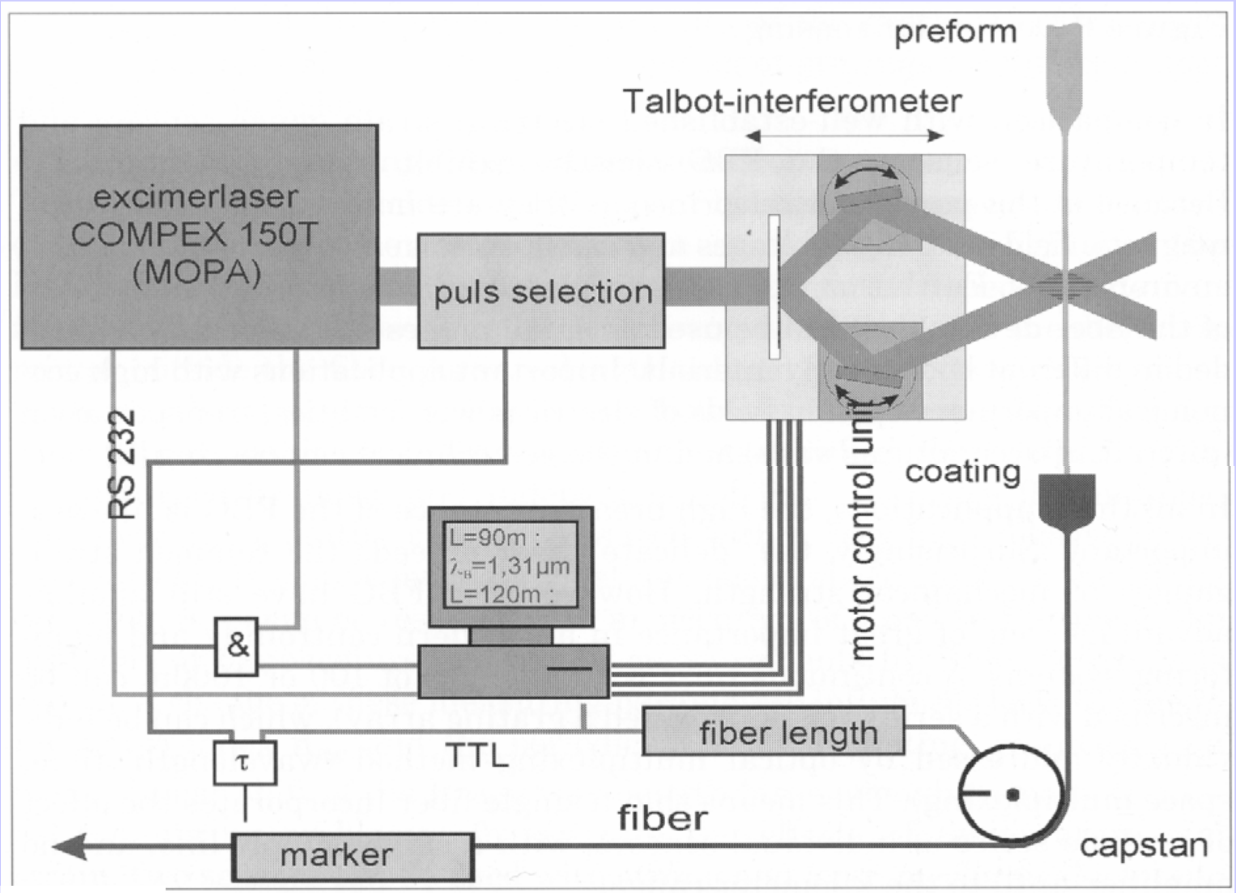
Example of a fiber Bragg grating (FBG), obtained by exposing the fiber to a UV pattern. Bragg gratings are characterized by Δn periods in the micro and submicron range. These one-dimensional gratings are now commercially available.



(Adapted from: *Introduction to DWDM technology*, S.V. Kartalopoulos, IEEE Press, 2000)

The imprinting of 1-D gratings in planar devices for IO is also important. However, due to the short device length, only a short grating length is possible and a large Δn ~ 0.01 is required to obtain high reflectivity as in long FBG's.

A very useful method is to write gratings directly during the preparation process on the draw tower, just above the coating unit, called *Dynamic writing*.



Dynamic writing of FBG's at the draw tower.[8]

(Adapted from: J. Kirchhof and S. Grimm, in, *Glass and the photonics revolution*, Glass Sci. Technol., 2002)

Thin planar (2-D) gratings are restricted to two dimensions either by the use of a *thin* photosensitive film, or by strong absorption of a bulk glass at the write laser wavelength, effectively limiting the light penetration to a depth of ~ 1/nα. Volume gratings (3-D) imprinted in thicker glass samples, on the other hand, may have application in holographic information storage.

Patterns and dimensions (D) of Δn structures and starting devices in which they are laser-written. Sample thickness is designated by d.

Δn structure			starting device		Refs.
type	dimen-sion	description	dimen-sion	description	
Bragg grating Λ ~ 0.5-5 μm	1D	fiber Bragg grating	1D	single-mode fiber	[1-17]
		channel waveguide Bragg grating		channel waveguide in planar device	[18,19]
	2D	planar or thin grating *limited to film dimension*	2D	thin film on substrate	[20-26]
		planar or thin grating *limited to exposed surface*		bulk glass with strong absorption at write laser wavelength	[27,28]
	3D	volume grating	3D	fiber preforms: d = 0.1-0.3 mm	[3-5,15,17]
				bulk samples: d = 1-7 mm	[29-44]
Long period grating Λ > 100 μm	1D	long period fiber grating	1D	single-mode fiber	[45-47]
Waveguides	1D	channel waveguide *limited to film dimension*	2D	thin film on substrate	[48-54]
		channel waveguide *limited to exposed surface*	3D	bulk glass with strong absorption at write laser wavelength	[55-57]
		channel waveguide *limited to focal point*		fs-laser-exposure	[58-63]
		channel waveguide *limited by self-writing*		bulk glass transparent at write laser wavelength	[64,65]
	>1D	multi-mode	3D	bulk glass transparent at write laser wavelength	[55,66]

(Adapted from: H.E. Heidepriem, in, *Glass and the Photonics revolution*, Glass Sci. Technol., 2002)

For *sensing* applications, the optimization of sensor gratings must be done in the following areas:

● high photosensitivity (especially for dynamic writing)

● compatibility with standard fiber (> [Ge] => > NA => < core dia. for single mode => > optical connection losses)

● low optical attenuation (> [Ge] and UV exposure => > optical loss)

● high mechanical strength and temperature stability

● reproducibility of fabrication

PS was first discovered in Ge-doped silica glass, which is known to contain the germanium-oxygen-deficient-center (GODC, a hole), absorbing @ 240 nm. A very efficient method to increase Δn by an order of magnitude, up to ~ 0.001, was found to be the treatment of Ge-doped silica-based fibers and thin films with H_2, the so-called H_2 loading. Fiber Bragg gatings were also produced in other silicate or HMFG, containing dopant ions such as Ce^{3+} and Ag^{+}.

The table below lists the main types of lasers used to study the PS phenomenon and to imprint Δn structures. Depending on the particular applications, cw or pulsed lasers are favored.

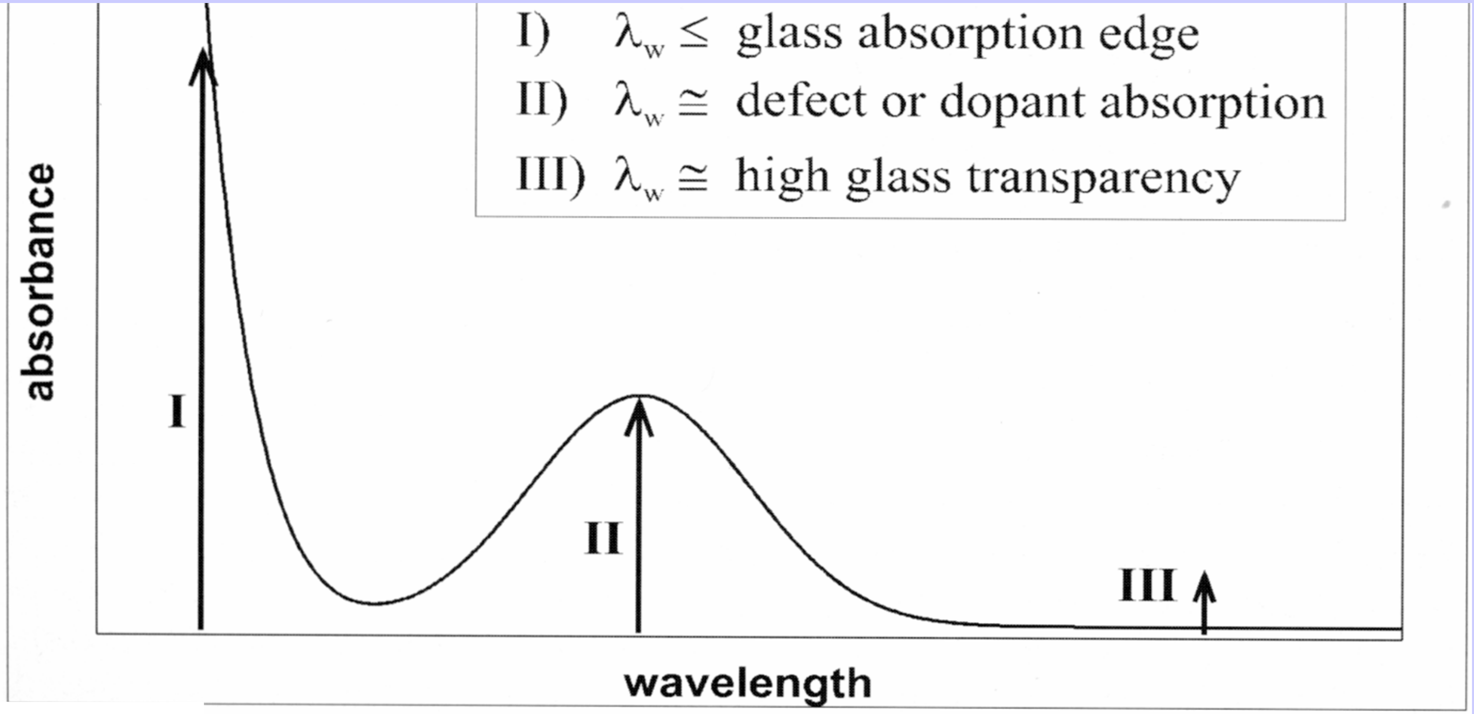
Lasers used for creation of photosensitivity.

spectral range	laser wavelength	laser type	regime
VUV	157nm	F_2	pulsed ~tens ns
UV	193nm	ArF excimer	pulsed ~tens ns
	244nm	Argon ion frequency doubled	cw
	248nm	KrF excimer	pulsed ~tens ns
	266nm	Nd:YAG frequency quadrupled	pulsed ~ tens ns
	325nm	HeCd	cw
VIS	455-488nm	Argon ion	cw
NIR	~800nm	Ti:sapphire	pulsed ~100fs

(Adapted from: H.E. Heidepriem, in, *Glass and the photonics revolution*, Glass Sci. Technol., 2002)

The figure shows the three possible relationships between the glass absorption and write laser wavelength. In regime I, of strong laser absorption, one-photon processes prevail and the laser-induced effects are restricted to a thin layer at the sample surface (of thickness ~ 1 / n α). Examples are Ge-doped silica glass illuminated at 157 nm, or HMFG irradiated at 193 nm.

In regime II, the laser is absorbed by localized defects or dopant states within the gap, as in Eu^{2+} or Ce^{3+} co-doped, Ge-doped silica under UV exposure @ 240-290 nm. In regime III, non-linear processes can create index changes, as for fs laser exposure of different glasses @ 800 nm, or 488 nm argon laser exposure of Ge-doped silica glass.



Schematic illustration of the relationship between glass absorption spectrum and write laser wavelength λ_w.

(Adapted from: H.E. Heidepriem, in, *Glass and the photonics revolution,*Glass Sci. technol. 2002)

PS mechanisms

Two basic models have been proposed to explain the occurrence of PS in glass.

The **color center model** is based on changes in the UV absorption at defect centers which originate refractive index changes, by one of two possible mechanisms: (1) photo-oxidation of GODC, Eu^{2+}, or Ce^{3+}, for ~ 250 nm irradiation; (2) sensitization by ions such as Tb^{3+} and Ce^{3+}, under 250 nm irradiation, where excited electrons are not fully removed from these ions and their de-excitation energy is released to the glass matrix, causing the formation of hole and electron defect centers.

In the **densification model**, for silica-based glasses, densification (or volume change) is accommodated by the photoelastic effect. In silica-based glasses, e.g., densification may result form the collapse of high-order ring structures into low-membered ones.

For example, densification plays a major role in Al-doped silica, whereas the color center model accounts for a major part of the PS in H_2-loaded Ge-doped silica.

In contrast to silica-based glasses, As_2S_3 and HMFG like ZBLA, having a more dense structure, exhibit photoexpansion due to widening of interlayer or interchain distances, which gives rise to negative Δn values.

Methods to characterize PS in glass

In gratings, the Δn modulation is determined from the reflectivity of FBG's, or diffraction efficiency of planar and volume gratings.

In planar waveguides, on the other hand, refractive index changes can be measured by prism coupling.

Information about defect centers and thus the contribution of the color center mechanism may be obtained from laser-induced absorption and electron spin resonance spectroscopies.