Sol-gel process: an overview

Ana C. Marques

Departamento de Engenharia de Materiais / ICEMS, Instituto Superior Técnico, TULisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA

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Sol-gel process: definition

Sol-gel process is a chemical route used to synthesize glassy or ceramic materials at relatively low temperatures, based on wet chemistry processing, that involves the preparation of a sol, the gelation of the sol and the removal of the liquid existing in fine interconnected channels within the gel.

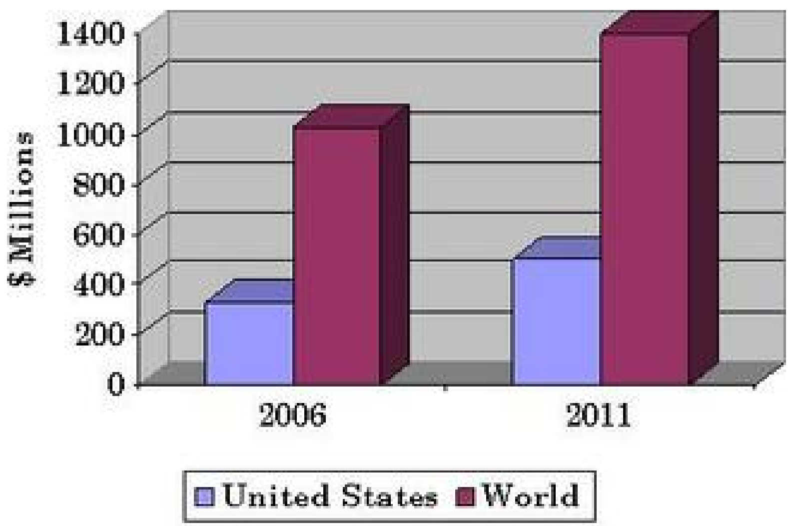
The growing interest of many researchers in the sol-gel method became apparent only in the mid-1970´s, with an increasing amount of published work since that time and, consequently, an increasing number of potentially attractive applications as high technology glasses and ceramics.

The first attempt to synthesize glass from gels was focused on silica, SiO_2.

"Sol-gel processing is a billion-dollar market" (Source: Laser Focus World)

According to a technical market report issued by BCC Research (Wellesley, MA), the U.S. market for sol-gel processing of ceramics and glass is expected to reach $500 million by 2011 at an average annual growth rate of 8.7%. The **global market** for sol-gel products in **2006 was $1 billion**; this is forecast to increase to **$1.4 billion by 2011 with an AAGR of 6.3%.**

Sol gel is a low-temperature method of fabricating glass in shapes that can range from simple to very intricate. High-quality optical elements are possible, as are doped materials (even containing organic dyes) suitable for laser-gain media. The U.S. has become the global leader in research and development. However, Japan is able to commercialize sol-gel technology and market products faster. European competition to the U.S. is mainly from Germany.



Homogenization of the different components in solution (**chemical precursors**, water, alcohol and **catalysts**)

- Metallic salts
- metal alkoxides, $M(OR)_n$
- organometallic compounds in which a metal M is directly linked to a C atom

Hydrolysis:

$M(OR)_n + H_2O \rightarrow M(OH)(OR)_{n-1} + ROH$

Condensation:

$2M(OH)(OR)_{n-1} \rightarrow (RO)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + H_2O$

$2M(OH)_n \rightarrow (OH)_{n-1}M\text{-}O\text{-}M(OH)_{n-1} + H_2O$

$M(OR)_n + M(OH)(OR)_{n-1} \rightarrow (RO)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + ROH$

Two different sol-gel processing routes are normally distinguished:

- **the *particulate* (or colloidal)**
- **the *polymeric route***

Solution
(of metal alkoxides)

Particulate route:

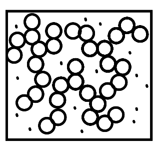
hydrolysis

Sol
(suspension of fine particles)

suspension of very fine, colloidal, non-polymeric particles in a liquid, with sizes between 1 nm and 1 μm

gelation

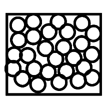
"Particulate" Gel



colloidal particles linked by van der Walls forces

drying

Dried Gel



firing

Dense Material

Polymeric route:

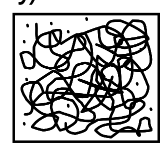
hydrolysis and condensation

Sol
(solution of polymer molecules)

solution of polymer molecules, in which the solid phase contains no dense particles larger than 1 nm, the lower limit of colloidal range

gelation (increase of viscosity)

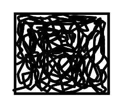
"Polymeric" Gel



covalent bonding between polymer molecules

drying / shrinkage of gel

Dried Gel



firing (heating, sintering, densification)

Dense Material

Advantages of sol-gel method:

- **Versatile**: better control of the structure, including porosity and particle size; possibility of incorporating nanoparticles and organic materials into sol-gel-derived oxides;
- **Extended composition ranges**: it allows the fabrication of any oxide composition, but also some non-oxides, as well as the production of new hybrid organic-inorganic materials, which do not exist naturally;
- **Better homogeneity**: due to mixing at the molecular level; **high purity**;
- **Less energy consumption**: there is no need to reach the melting temperature, since the network structure can be achieved at relatively low temperatures near T_g;
- Coatings and thin films, monoliths, composites, porous membranes, powders and fibers;
- No need for special or expensive equipment.

Drawbacks of sol-gel method:

- Cost of precursors;
- Shrinkage of a wet gel upon drying, which often leads to fracture due to the generation of large capillary stresses and, consequently, makes difficult the attainment of large monolithic pieces;
- Preferential precipitation of a particular oxide during sol formation (in multicomponent glasses) due to the different reactivity of the alkoxide precursors;
- Difficult to avoid residual porosity and OH groups.

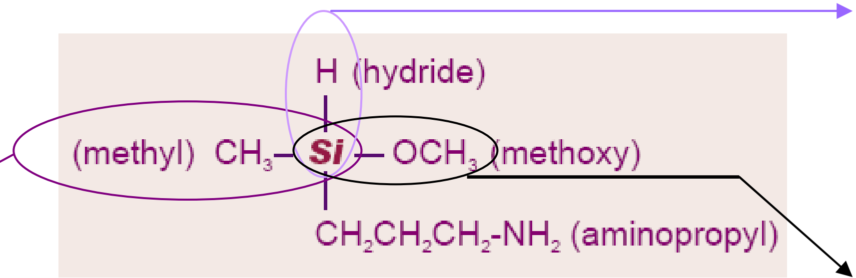
Metal alkoxides

Table. Representative metal alkoxides employed in glass preparation by sol-gel processing. Adapted from M. Yamane and Y. Asahara. Glasses for Photonics (Cambridge University Press, Cambridge 2000).

Alkoxide	*Formula*	*Boiling Point (°C/mmHg)*
Silicon ethoxide (TEOS)	$Si(OEt)_4$	168/760
Silicon methoxide (TMOS)	$Si(OMe)_4$	153/760
Boron n-butoxide	$B(OBu^n)_3$	128/760
Aluminium n-propoxide	$Al(OPr^n)_3$	205/1.0, 284/10.0
Aluminium n-butoxide	$Al(OBu^n)_3$	242/0.7, 284/10.0
Aluminium tert-butoxide	$Al(OBu^t)_3$	151/1.3, 185/10.0
Germanium ethoxide	$Ge(OEt)_4$	86/12.0
Titanium ethoxide	$Ti(OEt)_4$	103/0.1
Titanium tert-butoxide	$Ti(OBu^t)_4$	93.8/5.0
Zirconium ethoxide	$Zr(OEt)_4$	190/0.1

✓ silicon alkoxides are not very reactive : hydrolysis-condensation reaction rates must be increased by catalysts

✓ hydrolysis and condensation reactions of non-silicate metal alkoxides must be controlled by using chemical additives (complexing ligands, e.g. acetylacetone)



very reactive: it reacts with water to yield silanol (-Si-OH) species and, additionally, will add across carbon-carbon double bonds to form new carbon-silicon-based materials.

very reactive and hydrolysable methoxysilyl structure.

Organosilane: at least one carbon-silicon bond (very stable, very non-polar and gives rise to low surface energy, non-polar, hydrophobic effects)

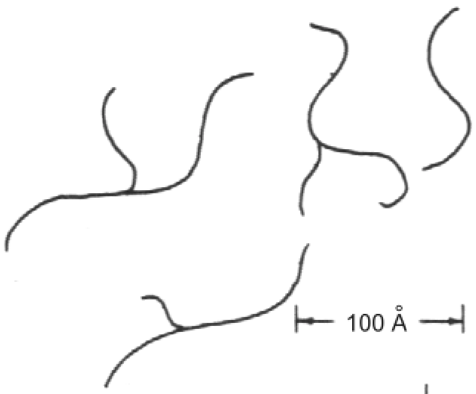
Characteristics of Various Organic Substituents on Silanes

Organosilanes R-Si(OMe)$_3$	
R	**Characteristics of "R"**
Me	Hydrophobic, Organophilic
Ph	Hydrophobic, Organophilic, Thermal Stability
i-Bu	Hydrophobic, Organophilic
Octyl	Hydrophobic, Organophilic
-NH(CH$_2$)$_3$NH$_2$	Hydrophilic, Organoreactive
Epoxy	Hydrophilic, Organoreactive
Methacryl	Hydrophobic, Organoreactive

(Source: Dow Corning, Silane-guide)

Acid and base-catalysis

acid catalyzed conditions (“polymeric” gel)



SOL
Far from gel point

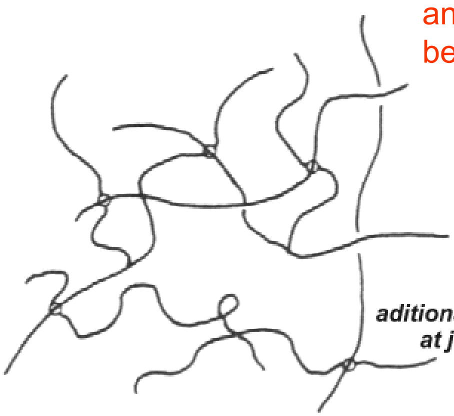
SOL
Near gel point

hydrolysis reaction is speeded up more efficiently than the condensation reaction

entangled primarily linear macromolecules

↓

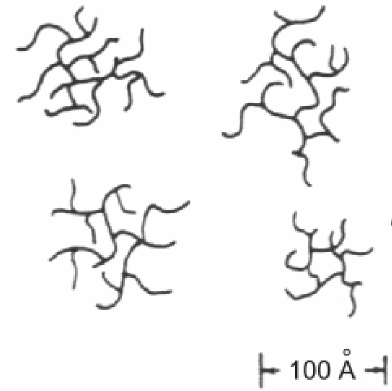
polymer chains are weakly cross-linked and the structure can be highly compacted before gelation



GEL POINT

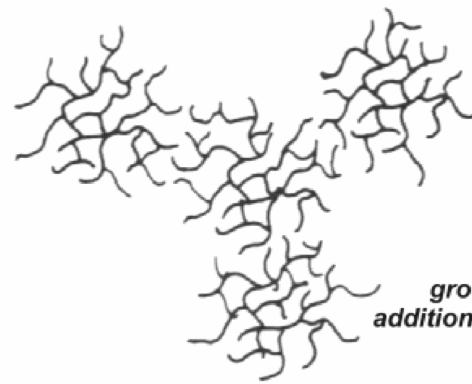
aditional crosslinks at junctions

base catalyzed conditions (“particulate”gel)



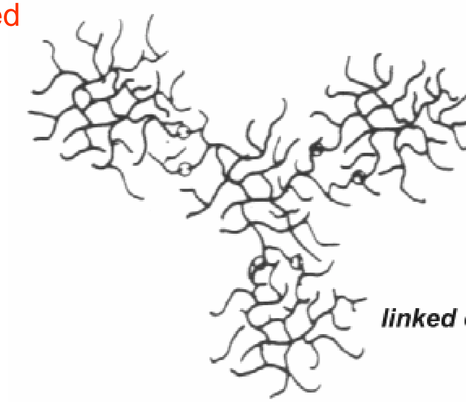
SOL
Far from gel point

branched clusters



SOL
Near gel point

growth and additional branching



GEL POINT

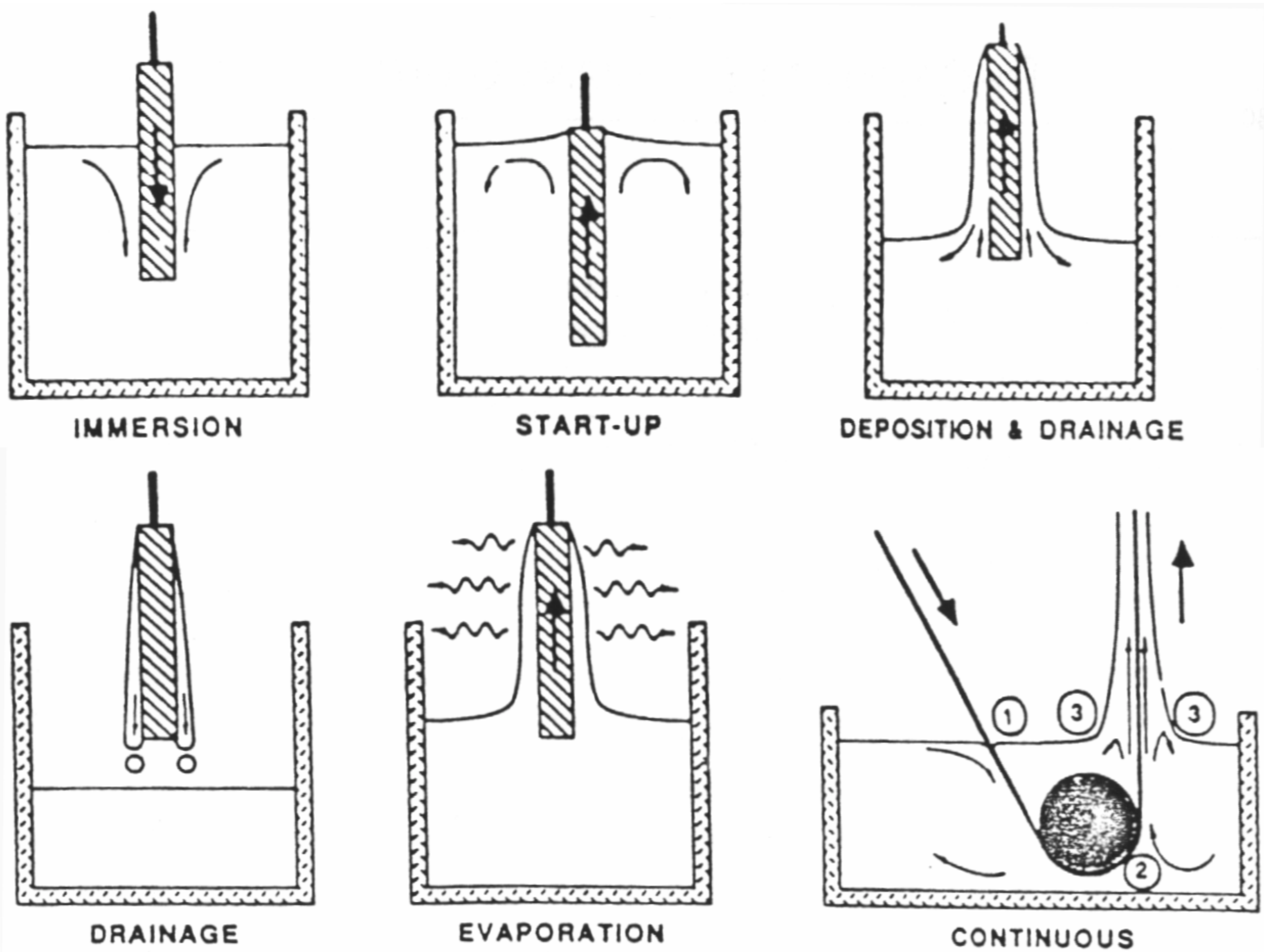
linked clusters

residual spaces in between the clusters

Coating methods

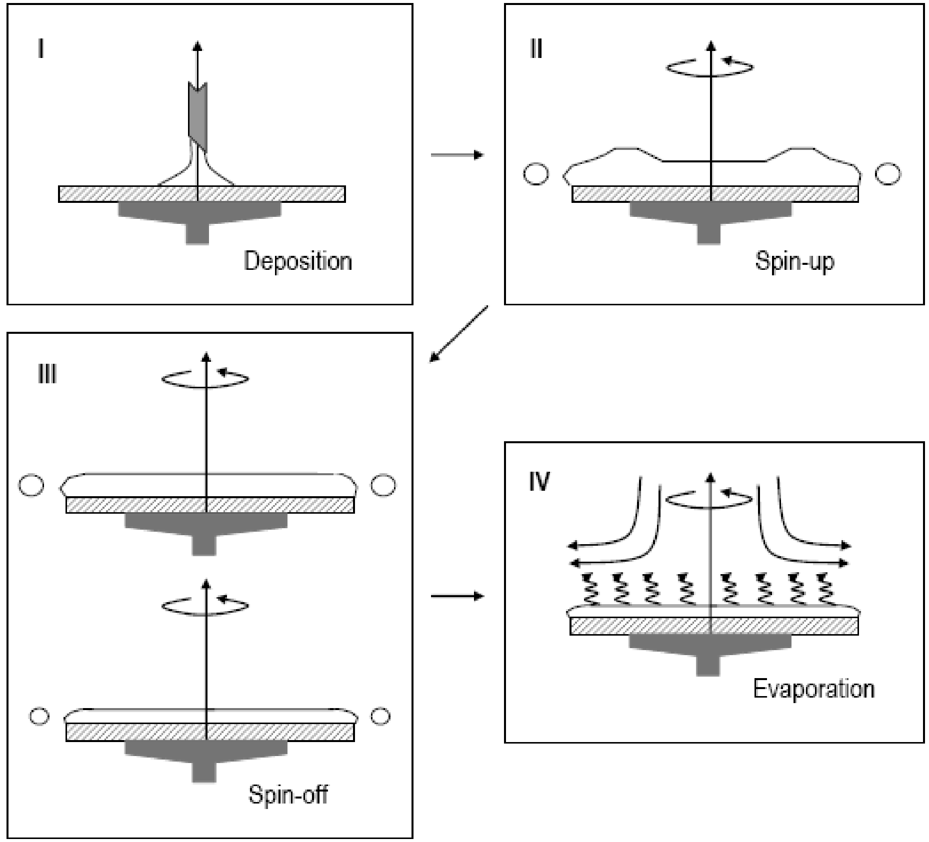
Dip-coating:

(The faster the substrate is withdrawn, the thicker the deposited film)



Industrial dip-coating system

Spin-coating:



Stages of the spin-coating process: (I) deposition, (II) spin-up, (III) spin-off and (IV) evaporation. (not to scale).

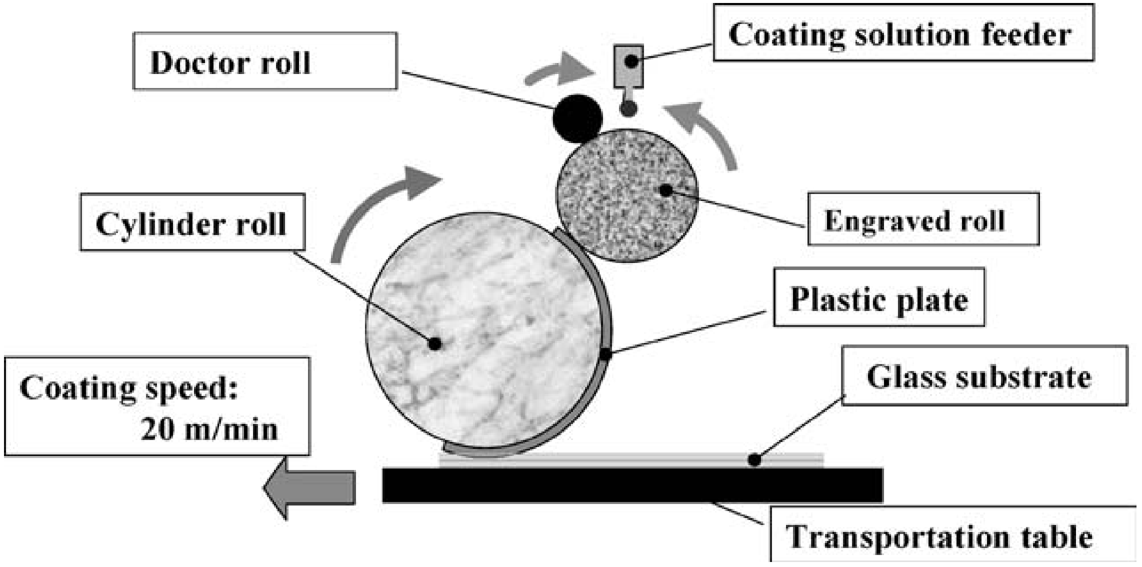
Thickness of the films depends on:
rheological properties of the solutions; the spinning conditions, such as spinning time, velocity and atmosphere, and the heat treatment time and temperature.

Other tecnhiques for thin film deposition onto substrates:

spray-coating

the surfaces are sprayed with fine disperse solutions.
Used mostly for protective coatings.

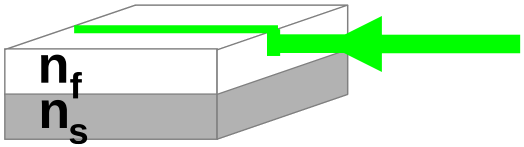
roll-coating



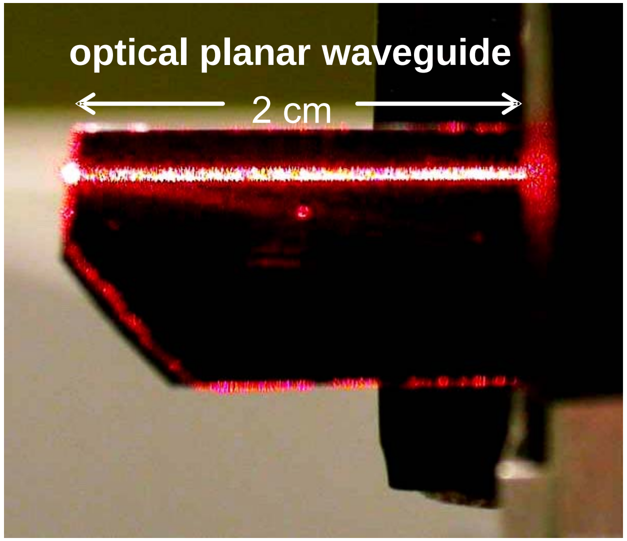
Applications

Thin films (multilayers) for optical planar waveguides (optical amplifiers)

Ana C. Marques *et al*., Glass Technology, 46, 2 (2005) 50; Rui M. Almeida *et al*., J. Sol-Gel Sci. Technol., 31 (2004) 317

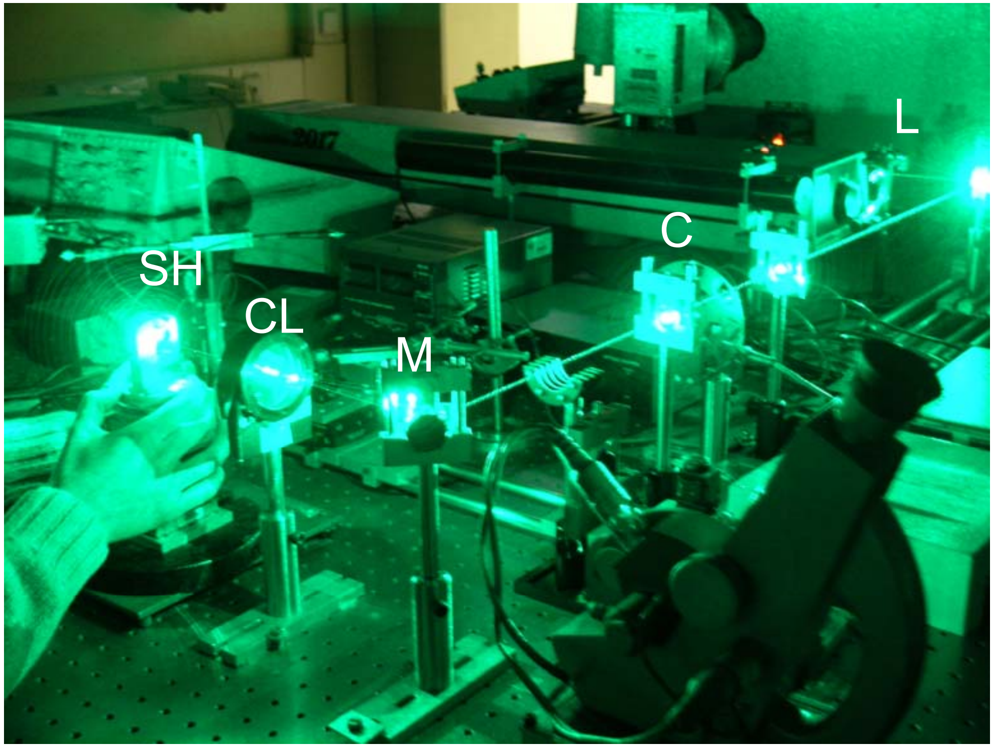


Multilayers for reaching desired thickness



Light propagation in a planar waveguide of composition SiO_2-TiO_2-Al_2O_3 (silica-on-silicon substrate; prism coupling).

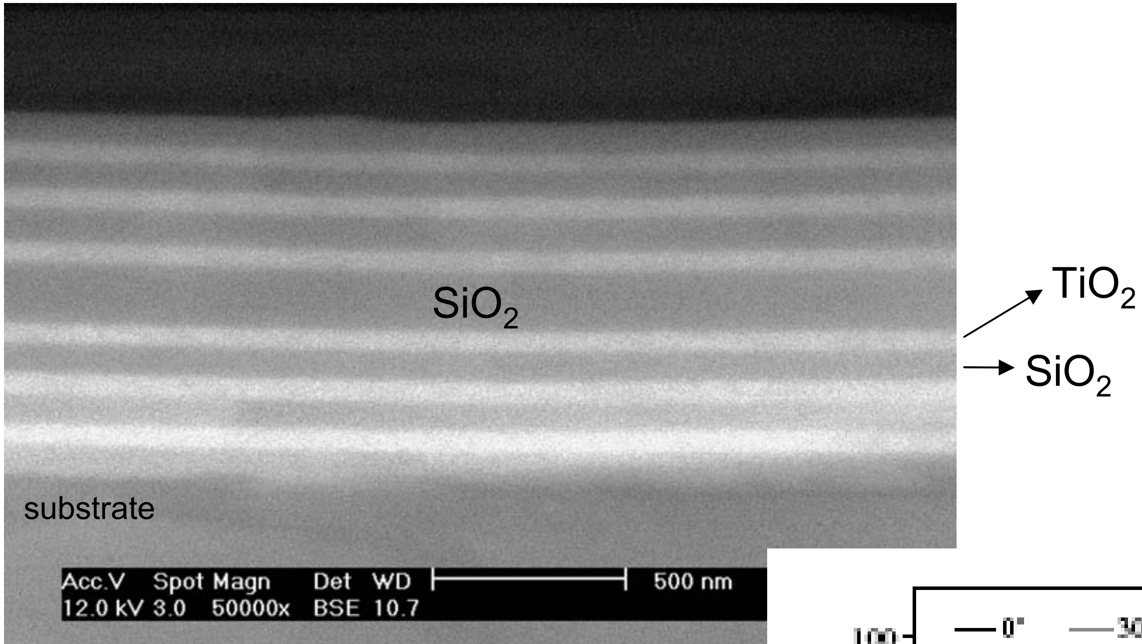
Optical propagation loss ~ 0.2 dB/cm.



Laser beam used for photoluminescence measurements (M-mirror, CL-convergent lens, L-laser source, C-chopper, SH-sample holder)

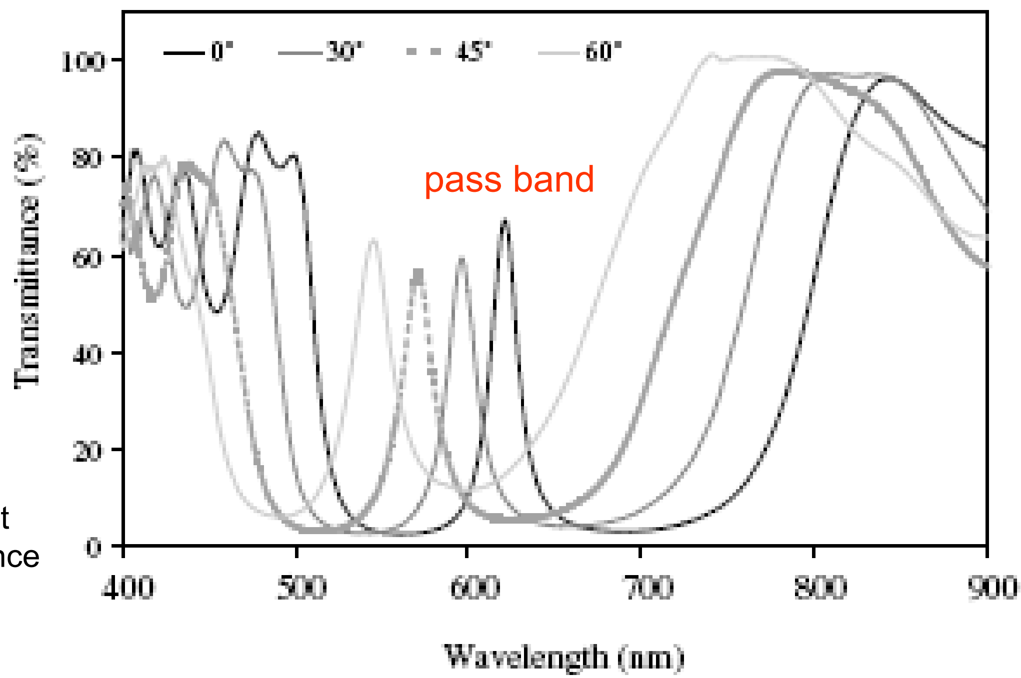
Photonic crystals (1-D): alternate layers of SiO_2 and TiO_2 with one or more defect layers

Rui M. Almeida, Ana C. Marques, J. Non-Cryst. Sol. 352 (2006) 475–482



FEG-SEM cross-section micrograph (backscattered electron mode) of a single Fabry–Perot microcavity with a silica defect layer (dark color).

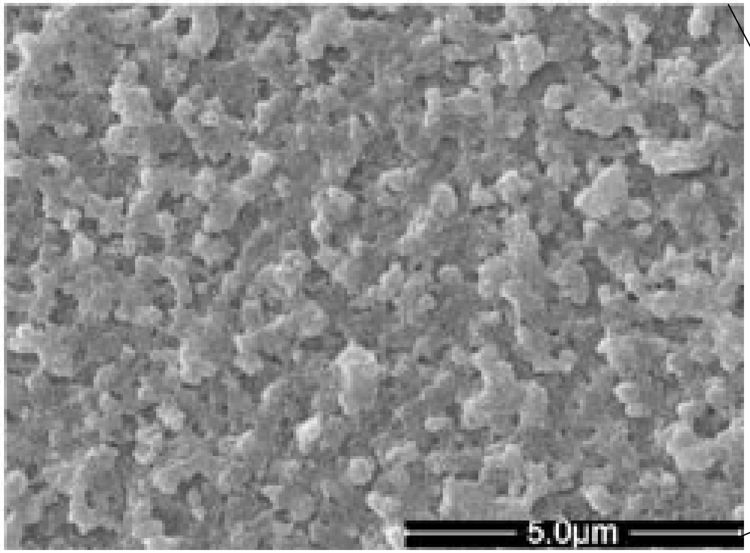
Interference filters: if one or more defect layers are incorporated
Mirror: if there are no defect layers (only stop band)

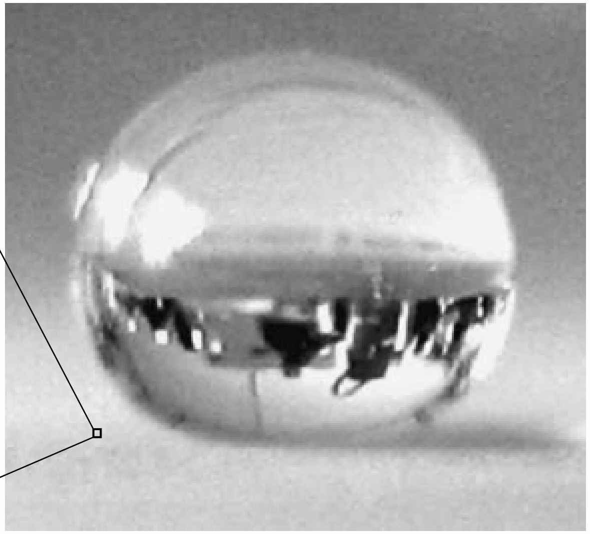


Visible–NIR transmission spectra of a single Fabry–Perot microcavity, for p-polarized (TM) light, at different incidence angles (off-normal).

Super-hydrophobic thin films by sol-gel and phase separation

H. Hou *et al*., J. Sol-Gel Sci. Technol. (2007) 43:53–57

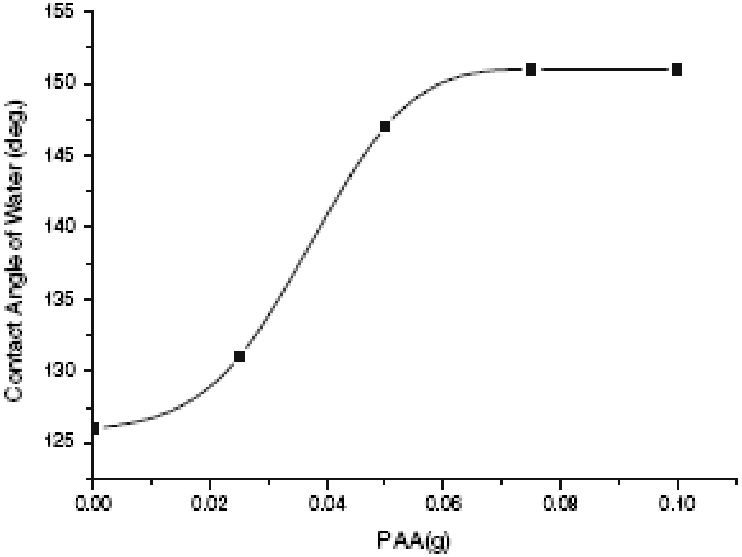




Thin films prepared with 0.075 g PAA. The contact angle for water was 151º.

The phase separation, induced by the addition of poly(acrylic acid) (PAA), originates the hill-like surface morphology: similar to the papillae surface morphology from natural surface of the lotus.

Surface roughness of films and contact angles of water droplets increase with increasing PAA concentration (up to 0.075 g).

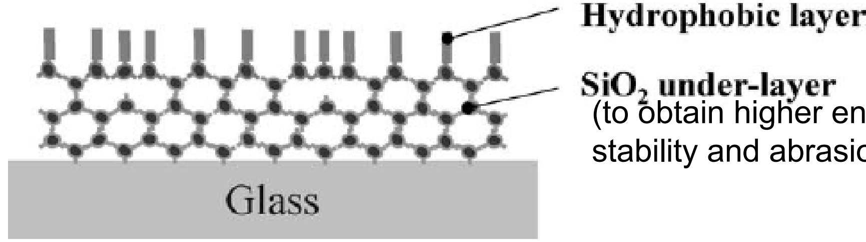


Commercial applications of the sol-gel process in Japan

Muromachi et al., J Sol-Gel Sci Techn (2006) 40:267–272

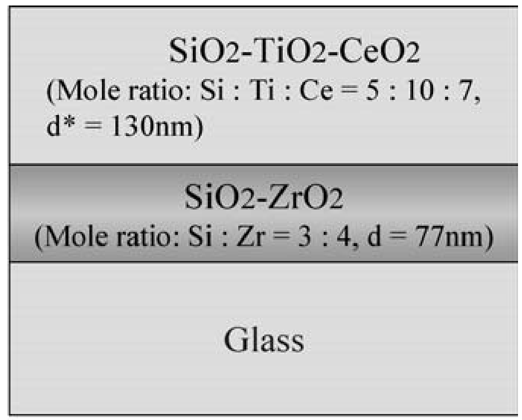
• Hydrophobic coatings

Hydrophobicity is provided by fluoroalkyl groups arranged in good order on film surface (contact angle for water: 100-108º)



(to obtain higher environmental stability and abrasion resistance)

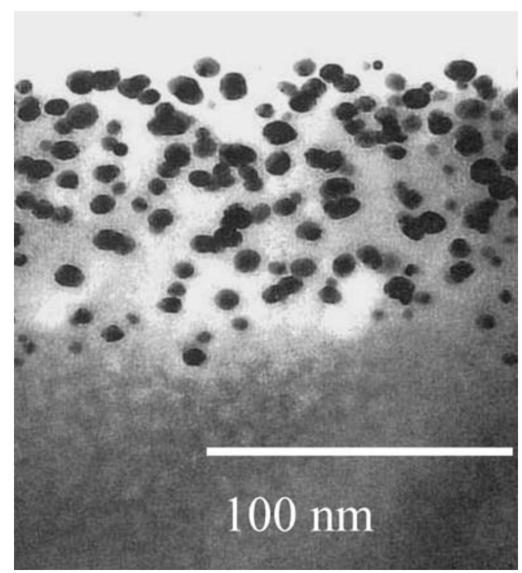
• UV absorbing coatings



(1)*: ‘d’ represents physical thickness.

• Colored coatings

The development of colored coatings with high visible transmission has been achieved e.g. using Au fine particles dispersed in the silica matrix.



• IR absorbing coatings, low reflective coatings, etc…

Advantages in terms of industrial process: feasibility of coating a large area; only small investment is required.

- Alkoxide-derived nanometer-sized silica

Yamane et al., J Sol-Gel Sci Techn (2006) 40:273–279

Silica nanoparticles used in the final polishing of silicon wafers for the fabrication of integrated circuits.
The particles are cocoon-like in shape and have almost replaced conventional abrasives because of the advantages over spherical particles of similar size in terms of obtaining high polishing efficiency for good surface finish.

- Treatment of paper with methyltrimethoxysilane

Yamane et al., J Sol-Gel Sci Techn (2006) 40:273–279

treatment of paper with an alkoxide solution for water repellent and oil resistance properties, which leads to new products for disposable tableware or cooking ware for microwave oven use.

Comparison of various materials used for the improvement of the properties of paper

Material	Property				
	Strengthening	Water repellency	Anti-oozing of oil	Thermal durability	Remark
Methyltrimethoxysilane	○	○	○	○	
Silicone	×	○	×	△	Good stripping quality
Acryl or Epoxy resin	△	△	○	×	
Florin-containing polymer	×	○	○	×	Releasing toxic compounds

• Antireflective coatings

The sol-gel dip coating process has also been used to **deposit thin films on large size plastic panels**. By developing sols with different refractive indices, multi-layer thin-film antireflective coating stacks were designed and fabricated. These coatings possess good uniformity and meet stringent automotive specifications. This technology has been commercialized successfully for **dashboard instrument panel** application in Toyota's new hybrid engine car, named Prius.

Inorganic and hybrid coatings for chemical protection of steels

Ana C. Marques, Janet Gallardo, Alicia Durán, Boletín de la Sociedad Española de Cerámica y Vidrio, 40, 6 (2001) 429.

Corrosion resistance of stainless steel can be enhanced through the application of SiO_2 coatings. However, these coatings are sensitive to alkaline attack, that produces the partial dissolution of the SiO_2 network…

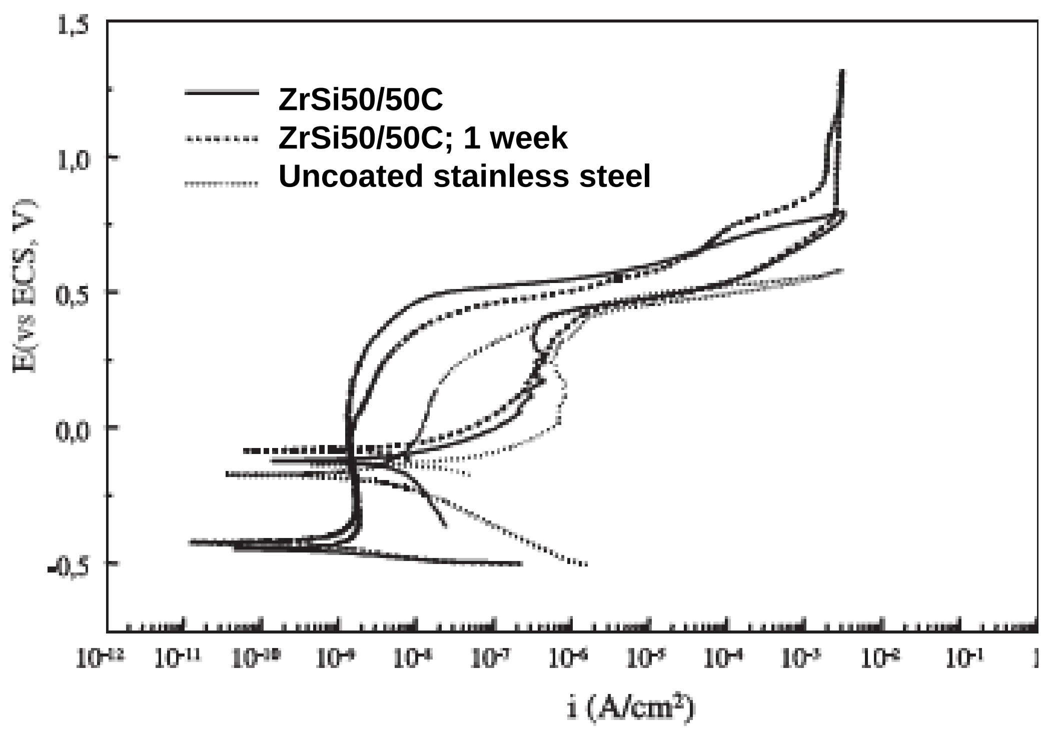
Composition: SiO_2-TiO_2 and **SiO_2-ZrO_2** **(precursors: MTES and TBOZr or TBOTi)**
dip-coating

The electrochemical resistance and coating stability were evaluated from **cyclic polarization tests in aqueous NaCl**, at room T, performed on **coated AISI304 stainless steel**.

Comparing the performance of stainless steel coated with 50%SiO_2-50%ZrO_2 to uncoated stainless steel:

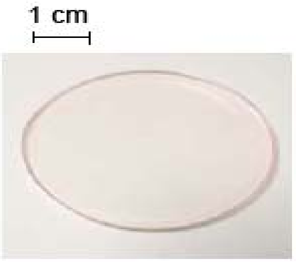
- Decrease of current density by one order of magnitude
- Larger difference between pitting potential (Ep) and repassivation potential (Er)

The coatings revealed a high resistance against alkaline media preserving an excellent electrochemical behavior in Cl^- rich solutions.



Bulk, dense glasses containing nanoparticles

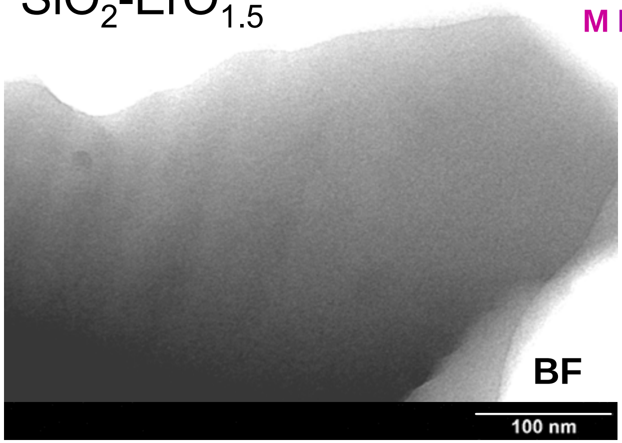
Ana C. Marques and Rui M. Almeida, J. Non-Cryst. Solids (2007, in press)



thickness ~ 2-3mm

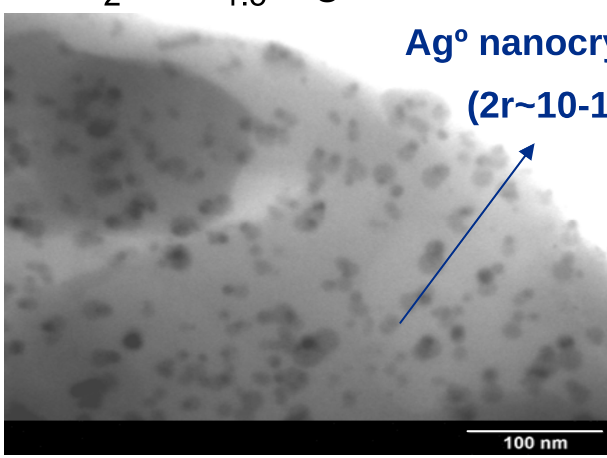
SiO_2-$ErO_{1.5}$

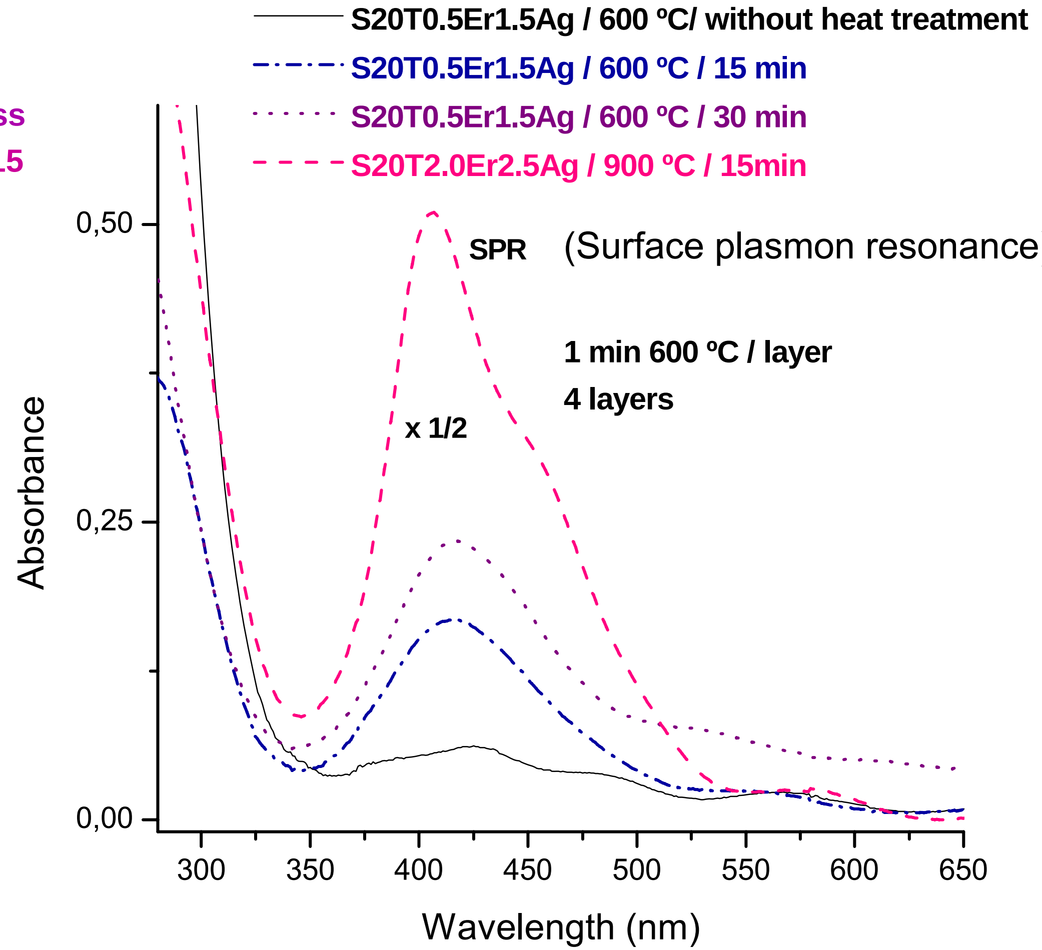
Er^{3+}-doped silica glass (pore doping with 0.15 M $Er(NO_3)_3$)



SiO_2-$ErO_{1.5}$-Ag

Ag° nanocrystallites (2r~10-15 nm)

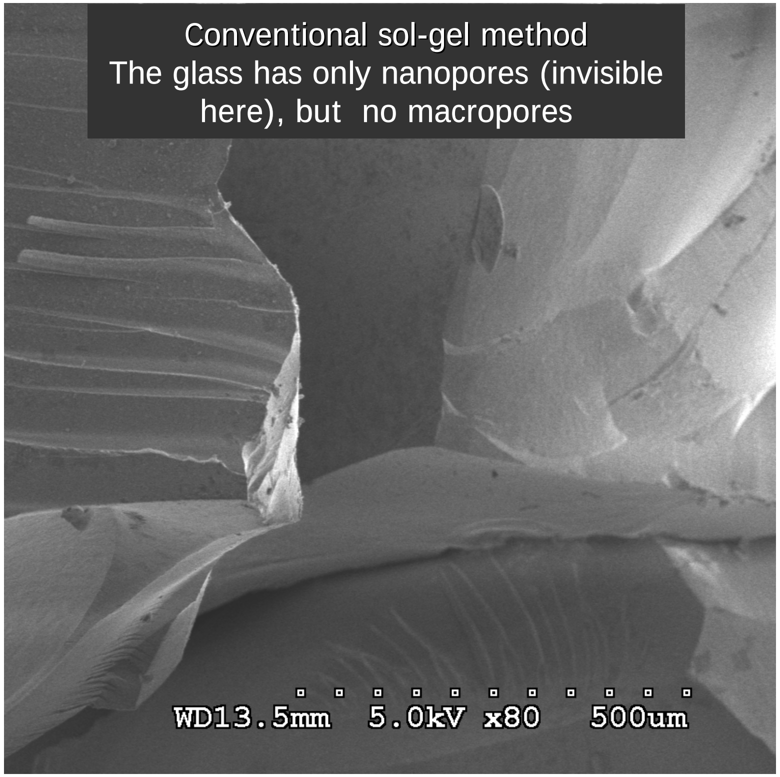


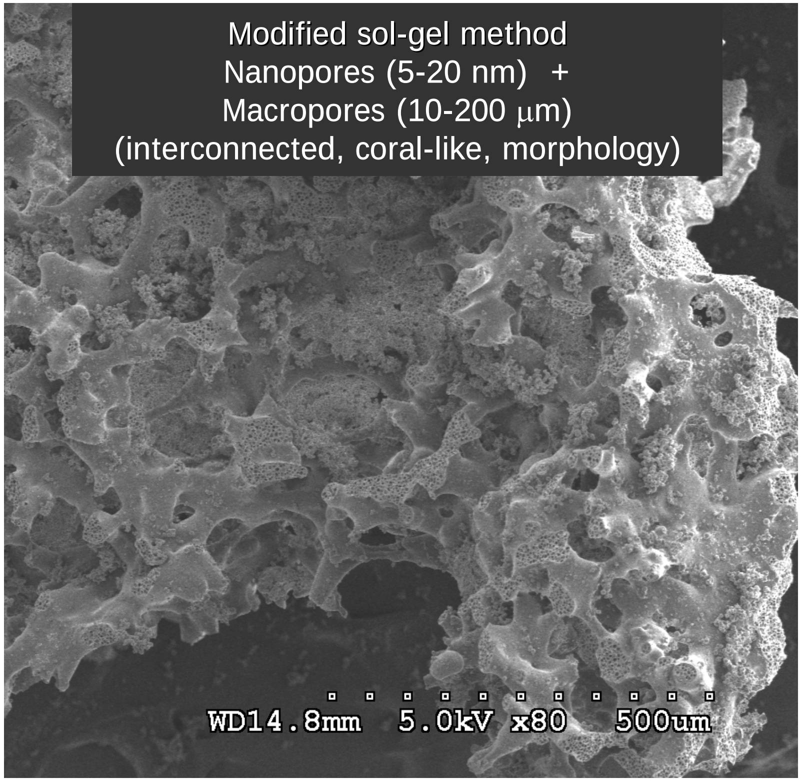


Er^{3+} and Ag°-doped silica glass (pore doping with 0.15 M $Er(NO_3)_3$ + 0.25 M $AgNO_3$ solution)

Bulk materials with hierarchical porosity at multiscale, using phase separation

Ana C. Marques, Himanshu Jain, Rui M. Almeida, Eur. J. Glass Sci. Tech. (in press) 2007.





Scanning electron micrographs of glass samples of composition 70% SiO_2 – 30% CaO (mol%), prepared by the normal (left) and modified (right) sol-gel technique

- ✓ bone scaffolds (Biomaterials)
- ✓ drug delivery
- ✓ catalysis
- ✓ hydrophobicity
- ✓ chromatography
- ✓ high-temperature applications

Conclusion

Sol-gel chemistry is still in its infancy and a better understanding of the basic inorganic polymerization chemistry is necessary in order to explore all the functionalities and possible applications of the process.

Sol-gel process is very attractive from the view point of small investment and new functions, although disadvantages such as sensitivity to process conditions should be considered.

versatility and purity…