

Sol–gel processing of materials for electronic and related applications

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Abstract. Various techniques of sol–gel processing for the preparation of electronic and related materials are described and reviewed. Typical examples are chosen from thin films and coatings of gels, crystalline materials and glasses as also bulk glasses to illustrate the variations in processing parameters and material properties.

Keywords. Sol–gel; electronic materials; coatings; silica glass.

1. Introduction

Because of the simplicity of operation and various important advantages, sol–gel processing has proved to be very popular in recent times for the preparation of inorganic materials. The major advantages of sol–gel processing that have attracted materials scientists and designers are: (i) ambient temperature of sol preparation and gel processing; (ii) high purity of precursors; (iii) product homogeneity; (iv) low temperature of sintering; (v) ease of making multicomponent materials; and (vi) good control on powder particle size and shape as also size distribution.

All of the above factors are attractive for the preparation of materials for optical and electronic applications. Sol–gel derived optical materials are enjoying a commercial market for more than three decades (Schroeder 1969; Dislich 1984), and many new materials are gradually coming into commercial production (e.g. Hench *et al* 1988; Kundu *et al* 1989; Sakka 1989). The advantages of the process in electronic applications are being realized relatively slowly, but a strong awareness is revealed by the current developments. Table 1 shows some of the materials for electronic and related application prepared by the sol–gel technique. This list excludes superconducting ceramic powders, coatings etc. because the information in the published literature is vast, and the subject demands a separate treatment.

Table 1 reveals, though only partially, that the materials in terms of both chemical composition and physical form are quite large in number, and it is nearly impossible to describe all the major achievements in sol–gel preparation of these materials within the span of a single article. We shall therefore pick up some examples out of this list and describe the preparative techniques adopted by various workers, the nature of the products obtained and the area of application with some recent results. However, before going into this, we shall describe in brief some of the main aspects of the sol–gel process for those readers who are not so familiar with this technique of material preparation.

2. The sol–gel processing technique

A sol has been defined as a suspension of fine particles of colloidal dimensions (1–1000 nm) in a liquid. In the classical sense, such particles may be generated inside the liquid by aggregation of molecular units (e.g. metal or metalloid particles in gold and

Table 1. Some examples of sol-gel derived materials for electronic and related applications (with typical sources of information)

Material	Application	Reference
<i>I. Films and coatings</i>		
TiO ₂	Photoanodes for water splitting; oxygen sensors	Yoko <i>et al</i> (1986, 1987b, c); Blum (1988)
WO ₃	Electrochromic devices	Unuma <i>et al</i> (1986)
BaTiO ₃ , SrTiO ₃	Ferroelectric films	Fukushima <i>et al</i> (1976); Yoko <i>et al</i> (1987a)
PZT, PLZT	Ferroelectric coatings in JFET devices	Fukushima <i>et al</i> (1984); Budd <i>et al</i> (1985); Dey and Zuleeg (1989)
ITO	Conductive infrared reflecting	Dislich and Hinz (1982); Gonzales-Oliver and Kato (1986)
Ta ₂ O ₅	Integrated circuits (replacement for SiO ₂)	Silverman <i>et al</i> (1986)
LiNbO ₃	Opto-electronic applications	Nashimoto and Cima (1991); Hirano and Kato (1988)
VO ₂	Switching (semiconductor-metal transition)	Speck <i>et al</i> (1988)
V ₂ O ₅	Antistatic coatings on photofilms	Livage (1985)
Silicate glasses	Coatings in MOSFET technologies	Weimer <i>et al</i> (1987) Warren <i>et al</i> (1988)
<i>II. Powders</i>		
TiO ₂	Dielectric ceramics	Barringer and Bowen (1982); Fegley Jr <i>et al</i> (1984)
ZnO	Varistor ceramics	Heistand II and Yee-Ho Chia (1986)
BaTiO ₃ , PLZT	Ferroelectric, Piezoelectric ceramics	Mazdiyasi (1982, 1984)
PbTiO ₃	Ferroelectric ceramics	Blum and Gurkovich (1985)
Cordierite	Packaging	Bernier <i>et al</i> (1986)
LiNbO ₃	Opto-electronic applications	Hirano (1988)
(Ti, Sn)O ₂	Dielectric ceramics	Hirano (1988)
<i>III. Gels/Glasses</i>		
TiO ₂ gel	Electrochromic displays, photoanodes	Livage (1986)
SiO ₂ and doped SiO ₂ glass	Substrates for semiconductor technology; optical communication	Clasen (1987, 1988); Rabinovich (1989); Mori <i>et al</i> (1988)

sulphur sols) or brought from outside (suspension of clay mineral particles in water). With the renewal of interest in the alkoxide-derived sols in recent times, the definition has been extended to include systems containing polymeric particles generated in alkoxide solutions via hydrolysis and polycondensation (see Brinker and Scherer 1989). The former is called a colloidal or particulate sol, and the latter, a polymeric sol. With time, sols tend to make a progressive journey towards a "gel" state, which is a semi-solid material containing a large amount of pores of different sizes which harbour some amount of the volatile materials (e.g. the dispersing liquid) used in the preparation of

the sol. In the case of colloidal or particulate sols, the gel stage is achieved simply by evaporation of the dispersing liquid when there is no strong interaction between the liquid and the solid phase; the particles come in near-physical contact and are usually linked by hydrogen bonding involving the surface hydroxyl groups or other weak bondings. When the particles have grown in the liquid, they exhibit Ostwald ripening, grow in size and finally come close to one another.

In case of polymeric sols, the polymers grow in three dimensions with continuing polycondensation reactions (unless restricted by imposed chemical conditions), forming innumerable clusters; finally, the clusters link up in forming a spanning cluster, leading to the generation of a stiff gel. Much before this happens, the sol is ready for coating on glassy and crystalline substrates usually by dipping, draining or spinning (Ganguli 1989), but sometimes also by spraying. On ageing, the sol coating forms a gel coating, which is then matured to an oxide coating by heating at temperatures in the approximate range 450°–700°C. When a bulk gel is required, the sol is allowed to gel in a container (the gel takes the shape of the container), and the gel allowed to dry slowly to avoid cracking. For obtaining bulk glass, the bulk dried gel is heat-treated under suitable atmospheres to cause sintering and densification.

An alkoxide sol is usually prepared by dissolving the alkoxide in a suitable solvent (generally in alcohol) and adding water slowly into it (or allowing it to react with atmospheric moisture) for starting the hydrolysis and polycondensation reactions. Chemical agents are often required in small quantities to control the reactions, e.g. to increase or decrease the rate of hydrolysis, or to increase the viscosity of the sol.

By changing the precursors and the method of adding one into another, very important changes can be brought about in the nature of the sol and the subsequent gel, e.g. the crosslinking of the polymeric clusters can be so much increased as to generate particles as dense as some colloids. Doping of compositions is usually done by adding salt solutions (nitrate, acetate, etc.) of the dopant cation into the sol; sometimes alkoxides are also used.

3. Coatings for electronic application

3.1 Titania and binary titanate coatings

Titanium oxide was one of the earliest materials to have been obtained in thin film form by sol-gel processing (Schroeder 1969). Typical procedures involve hydrolysis of titanium isopropoxide $\text{Ti}(\text{OC}_3\text{H}_7)_4$ or titanium ethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$; titanium butoxide, $\text{Ti}(\text{OC}_4\text{H}_9)_4$ is less preferred (Yoldas and O'Keefe 1984). The chemical parameters (in addition to the coating parameters) considered for controlling the coating thickness and quality are the equivalent oxide concentration of the initial solution, viscosity of the sol and the solvent for the alkoxide.

Following the demonstration by Fujishima *et al* (1969) that titania could act as an effective inert photoelectrochemical anode, there have been a series of investigations using sol-gel derived crystalline (mostly anatase) coatings of titania (Yoko *et al* 1986, 1987b, c). Utilizing the *n*-type semiconducting property, titania sol-gel coatings have been used in setting up photoelectrochemical cells in H_2SO_4 solutions of various concentrations. Under illumination (500 W Xenon lamp), the photoelectrochemical

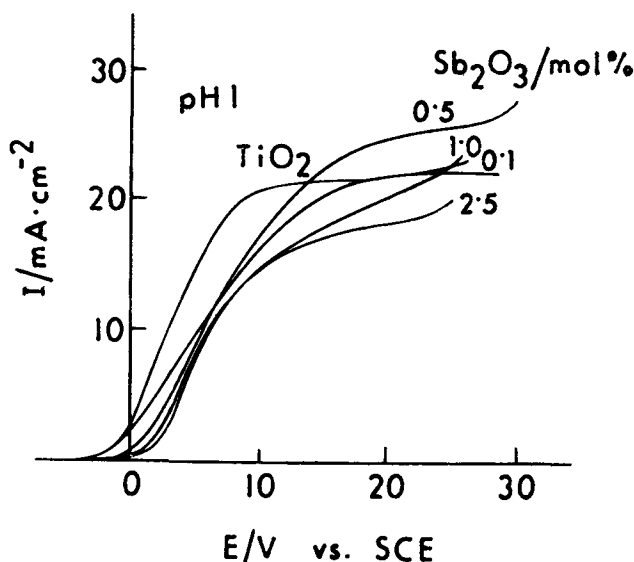


Figure 1. Development of photoelectrical current with Sb_2O_3 doped TiO_2 electrode in the form of sol-gel derived coating (after Yoko *et al* 1986, 1987a, b).

current was observed to flow at -0.5 to -0.3 V (vs SCE) and saturated above 0.5 – 1.0 V with concomitant evolution of the splitting products of water. It was also found (figure 1) that by an optimum doping of 0.5 mol% Sb_2O_3 , the photocurrent showed a significant increase (Yoko *et al* 1987c). Sol-gel derived TiO_2 coatings are also rated as a potential material for exhaust gas oxygen sensor devices (Blum 1988).

For the addition of a second component to prepare binary titanate films, several of which have important applications in electronics, the preparative procedures become a bit more complicated than in the case of pure titania. A flow diagram (figure 2) for SrTiO_3 (Yoko *et al* 1987a) serves as a case in point. Yoko and coworkers (Yoko *et al* 1987a) prepared films up to around 1800 nm by repeated dipping operation; crystallization was observed at 600 – 650°C . Fukushima *et al* (1976) reported the preparation of BaTiO_3 films from a complex sol containing a substituted Ti alkoxide and Ba naphthenate dissolved in butanol and water. Good crystallization of the film was obtained at 500°C .

3.2 Lead zirconate titanate and related coatings

With the addition of further components (e.g. for the preparation of PZT, PLZT etc.), the preparative methods become very elaborate and the reactions complex. For such complex systems, choice of reactants is guided by their solubility, reactivity, viscosity, decomposition temperature, etc. (Budd *et al* 1985). In an initial work on PZT, Fukushima *et al* (1984) used lead 2-ethylhexanoate, titanium tetrabutoxide and zirconium acetylacetonate dissolved in butanol as the initial reactants. Note that an acetylacetonate was used instead of an alkoxide (+ acetylacetonate) to avoid rapid hydrolysis and precipitation of the zirconate or other phases. Fused silica and platinum were used as substrates; good crystallization of PZT was obtained only at 700°C .

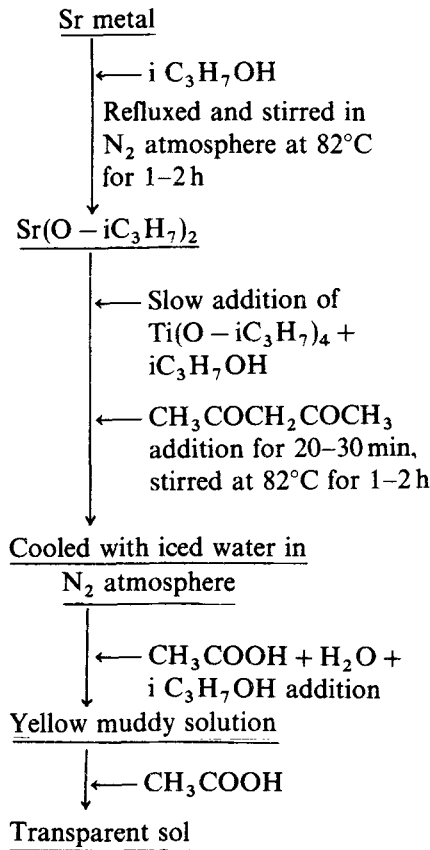


Figure 2. Flow diagram for the preparation of sols for SrTiO₃ coating (after Yoko *et al* 1987a).

Following this work, a series of investigations on PZT and related films was published during this period (e.g. Budd *et al* 1985; Guang-hua *et al* 1988; Shu *et al* 1988), and in many cases improved products were reported. A flow diagram (Budd *et al* 1985) for the preparation of PLZT is shown in figure 3. In a subsequent modification of the technique of homogeneous sol preparation, Takahashi *et al* (1990) suggested the use of lead acetate trihydrate as the source of PbO and diethanolamine (along with isopropanol) as the medium for complete dissolution of the acetate.

The success in obtaining good quality, well-crystallized PZT and related materials in thin film form at reasonable temperatures has encouraged materials designers to try them out as radiation hard and non-volatile ferroelectric CMOS static RAMs. In a recent development, Dey and Zuleeg (1989) have extended their work on ferroelectric PZT films by depositing them on III-V compounds (notably GaAs); the central idea is to study the compatibility of the sol-gel process for PZT film deposition with the GaAs planar and complementary JFET integrated circuit technology.

The electrical properties of sol-gel derived PZT and PLZT coatings have shown improvements with modifications in the processing technique, and the endeavours are still going on. The data shown below will give some idea of the ranges of values of some of the properties obtained by different authors cited in this section: Dielectric constant:

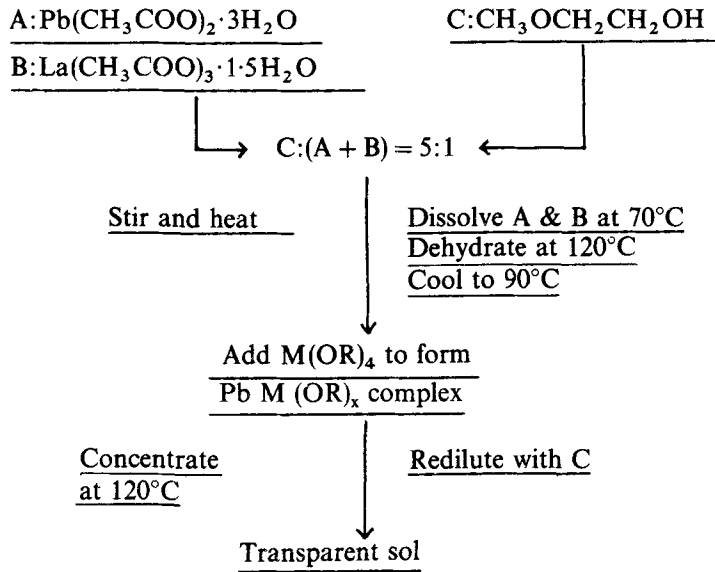


Figure 3. Flow diagram for the preparation of sols for PLZT coating (after Budd *et al* 1985).

300–500; dielectric loss angle ($\tan \delta$): 0.40–0.01; relative permittivity: 500–1200; saturation polarization ($\mu\text{C}/\text{cm}^2$): 36; remanent polarization ($\mu\text{C}/\text{cm}^2$): 30.56–1; coercive field (kV/cm): 80–26; dc resistivity ($\Omega\text{-cm}$) 6×10^8 ; polarisation reversal cycles: 10^{12} .

3.3 Miscellaneous oxide coatings

Recently, work was initiated (Weimer *et al* 1987) to examine the potentiality of sol–gel derived silica, barium alumino–borosilicate and alumina–silica glassy films in MOSFET technologies. Films deposited on (100) oriented *n*-type silicon substrates showed that some of the films had relatively low interface state densities, and were very good insulators. In a similar work, Warren *et al* (1988) showed the sol–gel derived oxide films on *n*- and *p*-type silicon, baked at 800°C, were excellent insulators, exhibited low oxide/silicon interface trap densities, and were radiation hard.

Another interesting material, prepared via a non-alkoxide sol–gel route, is V_2O_5 . Semiconducting V_2O_5 gel layers can be deposited by using a polymerizable polyvanadic acid solution obtained through ion exchange of Na^+ in a sodium metavanadate solution (Livage 1985). Such layers exhibit ohmic electrical behaviour and the conductivity, which is mainly electronic, increases rapidly with increase in the amount of reduced ions, i.e. V(IV). A suggested application is as antistatic coating on photographic films.

4. Silica glass

Silica glass is one of the very important supporting inputs in a host of electronic applications and in a variety of ways too. Well-known examples are glassware and

substrates in semiconductor technology and glass fibres in telecommunication. Some details are given by Fanderlik (1991).

The melting temperature of silica ($\sim 1720^\circ\text{C}$) is less than that of many of the refractory oxides; however, its high viscosity at the melting point reduces its workability to a great extent, and makes the preparation of high purity silica glass via the melting route a complicated and costly proposition. Fanderlik (1991) gives a detailed picture of the manufacturing techniques, all of which are complicated high temperature technologies. For by-passing the melt route, there have been numerous investigations on sol-gel preparation of silica glass since the mid-seventies. Success in these researches was limited because of the cracking problems arising mainly out of inadequate control on the porosity and the water or hydroxyl content of the precursor gels.

The last decade, however, has shown very intensive activities in the development of sol-gel technologies for manufacturing silica glass usable at high temperatures. Most of the patents covering this new sol-gel process have come from Seiko Epson, Japan and most published accounts from AT&T Bell Laboratories, USA, though the two processes have essential differences as described below. Other major inputs came from Hitachi, Japan and Philips, Germany. In the following, we shall present a brief account of the recent important attainments in this field, most of which, however, have had as their immediate goal the replacement of conventional silica glass by sol-gel silica glass in optical communication applications.

Nearly all of the early efforts and some of the very recent ones at the preparation of a sol-gel silica glass *usable at high temperatures* involved the use of only alkoxides of silicon (methoxide and ethoxide) as the source material for silica (e.g. Matsuyama *et al* 1984); for doping, the alkoxides of the respective metals were used (Susa *et al* 1990). Silica glasses of very high purity were obtained by using raw materials of ppb level impurity content, and heating the gels under suitable atmospheres.

Another route thoroughly investigated specially by research groups at AT&T Bell Laboratories, USA and Philips, Germany (see a summary of work by Rabinovich (1989), also Clasen (1987, 1988)) used fumed silica (spherical, glasslike fine silica particles obtained as the product of hydrolysis of SiCl_4 under oxyhydrogen or plasma flame) in the preparation of particulate silica sols. Gels were obtained from such sols by initial contact of the particles via hydrogen bonding involving surface silanol groups and then by the so-called "neck growth" phenomenon due to dissolution and redeposition of silica. However, such gels had limited green strength because of the thixotropic nature of the sol and large pore size after initial drying.

While the alkoxide-derived gels generally have small pores (say, 2–8 nm) leading to a high degree of probability of cracking during drying and densification, such gels also densify at a relatively low temperature (around 1000°C). However, elimination of micropores (which cause swelling at temperatures above 1000°C due to expansion of the entrapped gases and generation of water vapour due to OH–OH condensation) is considered to be a difficult problem, and it is not certain if such gels can be made free from micropores. On the other hand, particulate gels derived from fumed silica usually have large pores (around 15–500 nm) and require temperatures of 1300°C – 1500°C for dense glass formation. In spite of the disadvantages, both these processes of precursor gel formation have been examined critically for obtaining glass tubes or rods with very low OH and other impurities suitable for optical communication fibre drawing.

In a parallel series of investigations carried out at Seiko Epson, Japan (see paper of

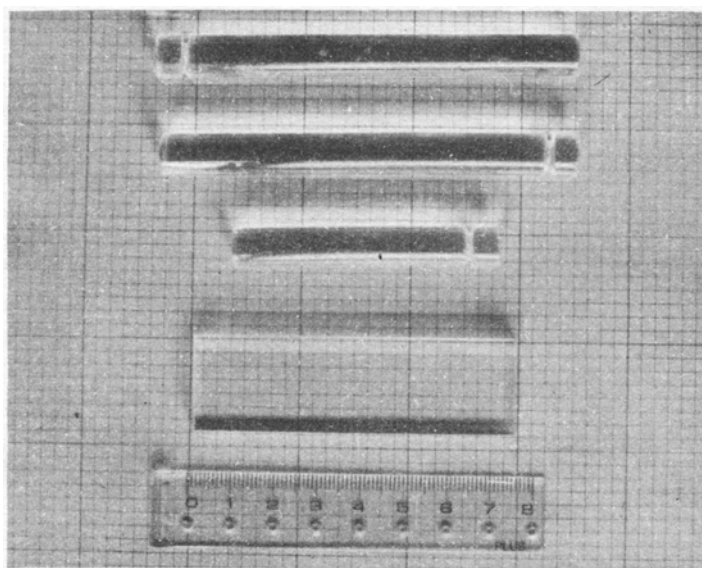


Figure 4. Sol-gel derived high-purity silica glass prepared at CGCRI.

Mori *et al* (1988) for a brief summary of work), leading to several hundred patent applications, a hybrid technique involving both silicon alkoxides and fumed or Stöber (Stöber *et al* 1968) silica was developed. The products had good geometrical tolerance and the required purity. The procedure has the following main advantages:

- (i) the gels produced by this technique have high green strength, and hence, offer easy handling and storage;
- (ii) they can be cut and ground before heating without generation of defects;
- (iii) the temperature of sintering to clear glass is lower than that in case of particulate gels.

On the above considerations, the Indian programme, sponsored by the Department of Electronics, Government of India at Central Glass and Ceramic Research Institute, selected the hybrid technique for the development of high purity silica glass. In this technique, preparation of the precursor gel comprises the following steps: (i) partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ with water; (ii) slow addition of fumed silica; (iii) ultrasonication of the sol; (iv) centrifugation and filtration; (v) casting in suitable moulds under static or dynamic condition; (vi) drying of the gel body thus formed under static or dynamic condition. Conversion of these gels to glass bodies is carried out by heating them through specific schedules to final temperatures of $1300^\circ\text{--}1500^\circ\text{C}$ under a variety of atmospheres (vacuum, oxygen, nitrogen, chlorine, helium). Following this route, low-OH and low-iron containing glasses are being prepared in various shapes e.g. rods, tubes, discs (see the paper by Kundu *et al* in this issue). Figure 4 shows some such sol-gel derived silica glass samples, matching in properties with their melt-derived counterparts.

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