Advances in Sol-Gel Technology

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Thin film or coating deposition represents the oldest commercial application of sol-gel technology. The first patent based on sol-gel processing was granted to Jenaer Glaswer Schott & Gen. in 1939 for silicate sol-gel films formed by dip coating. Coatings for rearview mirrors and anti-reflective and architectural applications have been in commercial production since the 1960s. Today, sol-gel thin film coatings are used extensively for such diverse applications as protective and optical coatings, passivation and planarization layers, sensors, high or low dielectric constant films, inorganic membranes, electro-optic and nonlinear optical films, electrochromics, semiconducting anti-static coatings, superconducting films, strengthening layers and ferroelectrics.

The sol-gel technique offers a low-temperature method for synthesizing materials that are either totally inorganic in nature or both inorganic and organic. The process, which is based on the hydrolysis and condensation reaction of organometallic compounds in alcoholic solutions, offers many advantages for the fabrication of coatings, including excellent control of the stoichiometry of precursor solutions, ease of compositional modifications, customizable microstructure, ease of introducing various functional groups or encapsulating sensing elements, relatively low annealing temperatures, the possibility of coating deposition on large-area substrates, and simple and inexpensive equipment. Within the past several years, a number of developments in precursor solutions, coating processes and equipment have made the sol-gel technique even more widespread.

Chemical Precursors

The sol-gel process uses inorganic or metal organic precursors. The most commonly used organic precursors for sol-gel film formation are metal alkoxides ($M(OR)_z$), where R stands for an alkyl group (C_xH_{2x+1}). Normally, the alkoxide is dissolved in alcohol and hydrolyzed by the addition of water under acidic, neutral or basic conditions, although film formation is also possible by the deposition of alkoxides followed by exposure to moisture. Hydrolysis replaces an alkoxide ligand with a hydroxyl liquid, as shown in ~~Equation 1~~.

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

Condensation reactions involving the hydroxyl ligands produce polymers composed of M-O-M bonds. In most cases, these reactions also produce the byproducts water or alcohol, as shown in the following equations, for silicon condensation:

$$Si(OR)_3OH + Si(OR)_4 \rightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + ROH$$

$$2Si(OR)_3OH \rightarrow (RO)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O$$

Further reactions lead to the formation of silicon oxides. The chemical reactivity of metal alkoxides is related to the R; the larger the R, the slower the hydrolysis of metal alkoxides.

Chemical precursors play a key role in the sol-gel coating by directly affecting the porosity, refractive index, hardness and other performance characteristics of the resultant coatings and thin films. In addition, the precursor is frequently a decisive factor for production in terms of cost and usability. Traditionally, the chemical precursors for sol-gel processes have been metal alkoxides, which are very moisture-sensitive (except silicon alkoxides) and require special handling environments. This limits the commercial applications of the sol-gel coatings. Recently, researchers have developed a more stable family of chemical precursors for sol-gel coating applications.* These polymeric metal alkoxides are not moisture-sensitive, are easy to use, and produce good coatings/thin films.

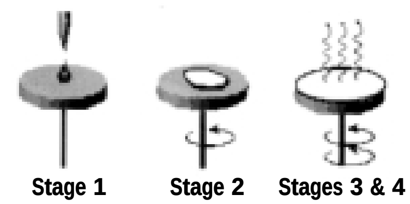

Figure 1. The four stages of spin coating.

Based on the success of these new precursors, other precursors have also been developed for use in sol-gel processes,

*These precursors were developed by Chemat Technology Inc.

including metal carboxylate, metal dialkylamides, amorphous and crystalline colloidal sol solutions, and organic/inorganic hybrids.

Sol-Gel Coating Processes and Coating Equipment

Several methods can be used to make sol-gel coatings with the sol-gel process. Spin coating and dip coating are two basic techniques used to deposit sol-gel coatings. Spin coating produces a one-sided coating, while dip coating yields a double-sided coating. Both techniques are used in manufacturing to make different coatings and thin films.

Roll coating is another coating technique and is widely used for industrial coatings, especially for flexible substrates. It can make coatings at a speed of up to 200 ft per minute.

Spin Coating. Spin coating is used for many applications where relatively flat substrates or objects are coated with thin layers of material. For example, several cathode ray tube (CRT) manufacturers use the spin coating method to make anti-glare or anti-reflection coatings. In spin coating, the material to be made into coating is dissolved or dispersed into a solvent, and this coating solution is then deposited onto the surface and spun off to leave a uniform layer for subsequent processing stages and ultimate use.

There are four key stages in spin coating (see Figure 1, p. 17):

- Stage 1: The deposition of the coating fluid onto the substrate
- Stage 2: Aggressive fluid expulsion from the substrate surface by the rotational motion
- Stage 3: Gradual fluid thinning
- Stage 4: Coating thinning by solvent evaporation

The coating thickness is inversely proportional to the square root of the rotation speed: thickness ~ $[1/\text{speed}]^{1/2}$. In addition, the coating solution properties (such as viscosity and liquid density) also affect coating thickness.

Some spin coating systems are specifically designed for depositing scratch-resistant coatings on ophthalmic lenses.** These systems have multiple functions, including cleaning, providing the solution, spin coating and curing (either thermal or ultraviolet). The temperature and atmosphere in the chamber environment can be precisely controlled to ensure high quality results.

Dip Coating. Dip coating is a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions. Vibration-free mountings and very smooth movement of the substrate is essential for dip systems. An accurate and uniform coating thickness depends on precise speed control and minimal vibration of the substrate and fluid surface. The coating thickness is mainly defined by the withdrawal speed, the solid content and the viscosity of the liquid. If the withdrawal speed is chosen such that the sheer rates keep the system in the Newtonian regime, the coating thickness can be calculated by the Landau-Levich equation:

$$h = 0.94 \cdot \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6}(\rho \cdot v)^{1/2}}$$

where h = coating thickness, v = viscosity, γ_{LV} = liquid-vapor surface tension, ρ = density, g = gravity. The schematics of a dip coating process are shown in Figure 2.

Dip coating processes are used for plate glass by Schott, based on developments made by Schröder[2] and Dislich[3,4]; for solar energy control systems (Calorex®) and for anti-reflective coatings (Amiran®) on windows. The dip coating technique is also used for optical coatings, such as on bulbs, and for optical filters or dielectric mirrors by various small and medium sized enterprises (SMEs) and other companies that must fabricate multilayer systems with up to 30 or 40 coatings with very high precision. A large-scale fused silica dip coating system (FSDCS) has been

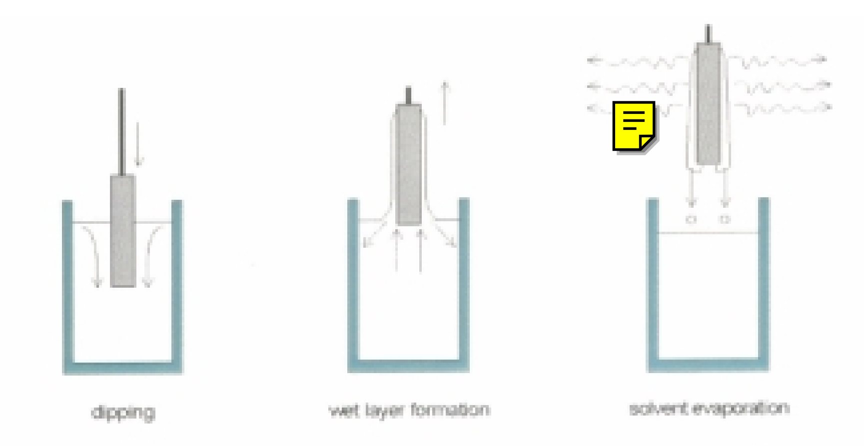

Figure 2. The dip coating process.

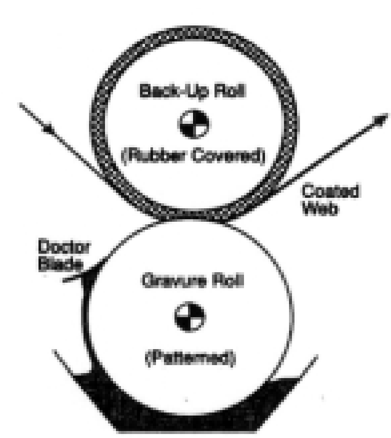

Figure 3. Gravure coating evolved from the printing industry.

**The Chemalux SR Coating System, supplied by Chemat Technology Inc.

delivered to Lawrence Livermore National Laboratory (LLNL) to make uniform anti-reflective sol-gel coatings over large precision optics measuring 44 cm x 44 cm x 41 cm and weighing up to 150 lbs. The FSDCS produces a speed ripple of less than ±1% at speeds of 2-20 cm/s, with strict control of vibration for both the optic and the tank.

One dip coating system† commonly used for sol-gel coatings incorporates atmosphere control, drying/curing, a programmable dip coating profile (withdraw speed, immersion time, etc.) and solution manageable tanks (temperature, filtration, etc.). Accurate speed control is obtained through the use of a proven precision, off-the-shelf motion system. Vibration control is enhanced by structural rigidity, isolation of the tank and motor drive, and spring mounting supports. Such a system is capable of achieving a uniform coating (±3% thickness variation).

Roll/Gravure Coating. Roll coating is a process by which a thin liquid film is formed on a continuously moving web or substrate by using one or more rotating rolls. Gravure coating is a roll coating technique that has evolved from the printing industry (see Figure 3). It is used to apply very thin coatings of low-viscosity liquids at high speed. Typical coatings are 1-50 μm thick, and the coating speed can be up to 15 meters per second.

The most important feature of a gravure coater is the patterned chrome roll. The pattern of cells or grooves is engraved onto the surface of the roll by mechanical engraving (knurling), chemical etching or electromechanical engraving. An excess of coating solution is applied to the gravure roll, which is then doctored by a flexible blade. The blade meters the cells partially full of coating liquid. The cells then pass into a nip where a fraction of the coating in the cells is transferred either to the web (in direct gravure) or to the offset roll (in offset gravure). In an offset gravure coater, the final transfer of coating to the web is at a second nip.

The main strength of gravure coating is the ability to apply thin coatings at high speed, with the coating thickness and uniformity controlled by the cell volume and cell uniformity. However, this method also has several drawbacks. Changing the coating thickness more than a small amount requires the gravure roll to be changed because the coating thickness is primarily determined by the volume of the cells on the gravure roll. Each cell must act like all the others, and the stability of the removal of the film from each cell is diffi-

†The DipMaster Dip Coating Systems, supplied by Chemat Technology Inc.

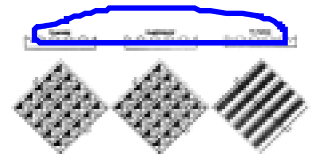

Figure 6. ~~I don't know which caption goes with this one~~.

cult to achieve at higher speeds and lower coating thickness. Additionally, wear of the gravure roll can be a problem when using abrasive coating formulations.

Several common patterns are used for gravure rolls, three of which are shown in Figure 7. Pyramidal and quadrangular patterns consist of rectangular cells, the former with a pointed bottom and the latter with a flat bottom. A trihelical pattern consists of equally spaced grooves that circle the roll, typically at a 45° angle to the roll axis.

This technique has been used to make anti-reflective coatings on plastic films. The resultant coating is uniform and shows good mechanical performance. The coating can be made at a speed of up to 250 ft per minute.

Developing a Turnkey Process

A number of oxides and organic/inorganic hybrid coatings can be deposited on substrates of metal, plastic, semiconductor materials and ceramics by the sol-gel technology. The key to successful applications of sol-gel coating technology is developing a turnkey coating process. The entire production process should be very well controlled by specifically designed equipment and integrated process procedures. The equipment should facilitate the coating process and avoid ambient environmental effects to a significant degree, if not completely. Automation can also be used to reduce human error. The combination of improved solution stability, proper equipment and automation can be expected to greatly improve the reproducibility of the sol-gel coating process and accelerate commercial applications. 🌐

Editor's Note

Additional figures and tables, including a list of polymeric metal alkoxide precursors and their applications, can be found with this article online at www.ceramicindustry.com.

References

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