PVD Processes: Glass as a Substrate Material

In PVD processing, glass is encountered as a substrate material in many forms. The most common are optical components, such as lenses, and plates, such as those used for mirrors and windows. Glass is an amorphous (vitreous) solid that has no long-range atomic order, but often has a short-range (near-neighbor) order. In glass, atoms or groups of atoms form a three-dimensional network that doesn’t have a repetitive order (i.e., polymerize). An element, such as selenium, can form a glass, but more commonly, glasses consist of network-forming oxide molecules, such as SiO₂, B₂O₃, GeO₂, As₂O₃, or P₂O₅. Silica (SiO₂)-based (silicate) glasses are the most common glasses. In silicate glasses, two SiO₄ tetrahedral ionic units. The tetrahedral shape can be visualized as being formed by three large oxygen ions (radius of O²⁻=1.32Å) in triangular coordination on a plane with the fourth oxygen ion on top, forming a pyramidal shape, and the small silicon ion (radius of Si⁺=0.4Å) in the hollow formed by the four balls in contact. The tetrahedral units then randomly polymerize into a three-dimensional network, forming the glass by joining at the apexes of pyramids but not along the sides. Glasses containing both SiO₂ and B₂O₃ are called borosilicate glasses (BSG), and those containing both SiO₂ and P₂O₅ are called phospho-silicate glasses (PSG).

The network formers are often combined with network-modifiers, such as Na₂O, K₂O, CaO, BaO, MgO, PbO, etc. Some network modifiers have large ions (radius of Na⁺=0.98Å), which act as substantial ions for the silicon and lower the bond strengths. The bond strength for Pb-O, for example, is 1.6 eV/bond. In the case of Al₂O₃, the aluminum ion is small (radius of Al³⁺=0.6Å), and it substitutes for silicon without lowering the bond strength appreciably, thereby forming aluminosilicate glasses. The Al-O bond strength is 4.4 or 3.4 eV/bond, depending on the coordination number.

The network modifiers change the properties of the glass, such as viscosity, index of refraction, optical dispersion, coefficient of thermal expansion, etc. The modifiers Na₂O and PbO decrease the viscosity of the glass. Architectural glass and blow-molded glass containers (so-called “soft glasses”), for example, may have the composition SiO₂=72-74 wt pct, Na₂O=12-15 wt pct, CaO=6-10 wt pct, MgO=3-5 wt pct and Al₂O₃=0.2-1.5 wt pct, and are called sodium silicate or soda-lime glasses. A high-lead (lead-silicate) glass, such as is used in cut-glass crystal, may have 25-50 wt pct PbO, which gives a low viscosity at relatively low working temperatures so that it can be easily molded.

The fictive temperature of a glass is the temperature above which mass movement will allow atom rearrangement. The fictive temperature is not a set temperature, but varies with the cooling rate. Glasses are metastable materials that are cooled through their fictive temperature before crystallization occurs. If cooled slowly, the material may crystallize. For example, the silica tetrahedra, which form a fused silica glass, can also crystallize into crystalline quartz if cooled slowly. Many glasses can crystallize (devitrify) over long periods of time at elevated temperatures.

Glasses can develop a high internal stress during fabrication, particularly if the glass has a high coefficient of thermal expansion. After fabrication (working), glass items are often reheated to relieve residual stress. The annealing temperature for a glass is defined as being the temperature at which the glass has a viscosity of 10ⁱ⁴ poises. At that temperature the internal stresses will be substantially relieved in 15 min, though the amount of stress relief will depend on the thickness of the glass. The strain point of the gas is defined as being the temperature at which the viscosity is 10ⁱ⁴. At that temperature, the stresses will be substantially relieved in four hr. The softening point of a glass is at a viscosity of 10⁶ poises, while the working temperature is when the viscosity is less than 10⁷ poises. The working temperature of a typical soda-lime glass, for example, is above ~750 °C, and the annealing temperature is ~500 °C. For fused silica, the working temperature is ~1600 °C, and the strain point is 990 °C.

The composition of the glass determines the coefficient of thermal expansion (CTE), which is an important consideration in many applications. Glasses can be formulated to meet the CTE required to match that of other materials. Borosilicate glasses, for example, have CTEs of about 4.5 x 10⁻⁶ cm/cm/°C and high phosphate glasses can be formulated to match the CTE of aluminum, a metal with a very high CTE (~28 x 10⁻⁶ cm/cm/°C).

The chemical composition of the surface of a glass can be different from that of the bulk of the glass. The difference can occur during solidification where some material is enriched at the surface, or it can occur with time. In high-lead glasses, lead will diffuse to the surface over a long period of time, forming a lead oxide layer. This enriched surface layer was the source of the development of a natural anti-reflection (AR) coating on “old” camera lenses before the use of deposited AR coatings.

The harmonica is a musical instrument that is played by rubbing wet fingers on the lips of rotating glass bowls. Lead poisoning was a problem to the harmonica musician in the early 1800s.
when lead glass was used for the bowls; now fused silica is used for the bowls. Optical glass is often formed by grinding and polishing. The polishing operation can leave polishing material, such as cerium oxide, embedded in the glass surface.

Glass will react with water vapor to form a hydrated surface layer that will increase in thickness with time. This hydrated surface layer is generally more brittle than is the surface of newly formed glass. The surface composition of a glass can be changed by improper handling. For example, if the fused silica glass envelope of a halogen lamp is contaminated by sodium from fingerprints, the sodium will diffuse into the glass at the high operating temperature and the glass may “soften” and deform during operation.

The strength of glass is not a fixed property but, as Griffith showed in 1920, is controlled by flaws, such as scratches in the surface. Flaws can be introduced into the glass surface by corrosion, abrasion, grinding or by the deposition of an adherent film with a high tensile stress. Glass can be strengthened by generating a high compressive stress in the surface of the glass. This is generally done by tempering. In the tempering process, the glass is heated well above its annealing temperature. Then the surface is rapidly cooled below the fictive temperature while the center is still hot. As the plate cools down, the material in the center would like to contract more than the surface, but is constrained by the rigid near-surface region. This puts the center of the plate tensile stress and the surface region under compressive stress. When the maximum compression is obtained without internally fracturing the glass, the plate is called fully tempered. Less than fully tempered glass is called strengthened or toughened glass. The compressive stress in the surface can also be generated chemically by substituting large ions such as K⁺ (radius=1.33Å) for smaller ions such as Na⁺ (radius=0.98Å) in the surface region by diffusion into the surface from a molten salt at a high temperature. When fully tempered or strengthened glass is fractured, it breaks into small pieces called shards and not into large jagged fragments, as does unstrengthened glass. For this reason, tempered or strengthened glass is used in such applications as shower doors.

The glass for optical lenses is often chosen for its index of refraction and optical dispersion, which is the sensitivity of optical properties to wavelength. For example, crown glasses, which are typically soda-lime glasses, have a low index of refraction and low dispersion, and flint glasses, which typically have a high PbO content, have a high index of refraction and high dispersion. The spectral transmittance can vary widely in the infrared. Soda-lime glass strongly adsorbs wavelengths longer than four microns, which is the most intense radiation from a black-body at 500 °C, while fused silica (often mistakenly called fused quartz) transmits well into the infrared, and is used for envelopes in tungsten-filament radiant heaters. This is an important factor in heating glass substrates using radiant energy in PVD processing.

Until 1959, plate glass was generally formed by rolling soft glass, often followed by polishing to improve the optical properties. In 1959, Pilkington patented the float glass process, which is now the most widely used technique for forming large-sized optical-quality glass plate. In the float glass process, molten glass is fed onto the surface of molten tin and spreads out, giving smooth surfaces on both sides of the plate as it cools. In a typical float glass plant, glass plate 0.25-in. thick is continually formed at a rate of ~3000 ft/hr and a width up to about 10 ft. In a typical soda-lime float glass plant, the raw materials are melted at ~1600 °C, poured onto the molten tin at ~1100 °C and passed onto rollers at ~600 °C. This results in an atomically smooth surface.

Glass formed by the float glass process has had one side in contact with the molten tin (tin side), and tin diffuses into the surface, giving a surface layer containing a high tin oxide content that can extend several microns into the surface. This side can be identified using UV radiation because the tin oxide fluoresces under the UV. The top surface (atmosphere side), which sees an inert or reducing atmosphere, is depleted in alkali and enriched in silica. In some cases, deposited PVD films will nucleate differently on the two sides of the float glass because of their different compositions. Common defects in glass include regions of nonuniform composition, solid inclusions called stones, and bubbles of gas called seeds. Stones of NiS are notorious for causing spontaneous failure when fabricating fully tempered glass. Glass can also contain metallic ions, which lend color to the glass. Examples are: Cr⁺ for green, Mn⁺ for purple, Fe⁺ for yellow and Co⁺ for blue. Iron is often an impurity in soda-lime glass.

Glass surfaces can be corroded by the environment. Alkaline water, in particular, is a strong corrosive agent. Glass should be stored in such a manner that water does not condense and remain on the glass surface, because the condensed water leaches alkaline material from the glass and becomes progressively more corrosive. The corrosion products are typically calcium and sodium carbonates that can be removed by acid washing. The best material for separating glass sheets in storage is PMMA beads loaded with an adipic acid, although styrofoam beads, paper, sawdust and many other materials are often used.

Glass can be formed into shapes by cutting, grinding, rolling, pressing, slumping (sagging) into or over forms, and blow-molding into forms. Glasses are also used for coatings by flowing molten glass over the surface of metals (enameling) or ceramics (glazing).

Glass films can be deposited by PVD processes by evaporation or sputtering glass source material, quasi-reactive deposition by vaporization of the condensable materials in a reactive plasma. The coefficient of thermal expansion of PVD-deposited glass can be an important property, because differences in CTE between the film and the substrate materials, as well as the nature of the film growth, can give high residual stresses in the high-modulus glass films. Generally, the deposited glass films should be annealed after deposition, but this can be a problem unless the CTE of the film matches that of the substrate material. The CTE is also important in the PVD processing itself. Pure silica (SiO₂) glass, for example, has a very low CTE (~0.6 x 10⁻⁶ cm/cm/°C) and is not susceptible to thermal shock. It is used in the RF sputter deposition of SiO₂ from an SiO₂ target. Glasses that have a high CTE are difficult to sputter at a high rate, because thermal gradients cause the sputtering target to fracture when it is heated unevenly or is stressed by the holding fixture. In the semiconductor industry, phospho-silicate glasses (PSG) for encapsulation are deposited by plasma-enhanced chemical vapor deposition (PECVD).

**Bibliography**