

Display Glass

45. Display Glass

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Active matrix displays are rapidly making all other display technologies on the market obsolete. They are all around us, from the smart watches on our wrist, to the phones in our pocket, to the TVs in our homes and they provide us with information, entertainment, biometrics, and a connection to the world, all on a thin bright device. The array of thin film transistors in the backplane of all active matrix devices eliminates cross-talk between pixels, provides a larger dynamic range in brightness, and accelerates the response time of the display. Whether it be a liquid crystal display (LCD) or an organic light emitting diode (OLED)-based display, an efficient and responsive active matrix of thin film transistors requires high mobility silicon, which requires high processing temperatures and precise patterning. This puts great demands on the glass substrate that the transistors and the entire display are built upon. The glass must be incredibly flat, smooth, and dimensionally stable at temperatures that would sag common window glass in a heap. This chapter will explore the amazing melting and forming technologies that have been developed to produce precision display glass sheets as well as the glass compositions that are the foundation for glass forming and device fabrication.

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45.1 Overview of Display Technologies

Displays have evolved from being a luxury item in the early days of cathode ray tube (CRT) televisions to a virtual necessity in the modern world. Due to the wide breadth of display applications, from televisions to car dashboards to phones and tablets to wearables, current displays employ a range of technologies. While a vast array of display technologies exist, many (such as CRT, passive matrix LCD, electroluminescent and plasma displays) are very mature, and innovation around the glass substrates used in those applications has slowed or ceased. CRTs dominated the display market for 75 years, from their monochrome introduction in 1922 for oscilloscopes and radar, to black-and-white TV in 1931, to color in 1953, to large screens in the 1980s [45.1], until lighter, thinner, and more efficient LCD flat screens started replacing them around the turn of the century and ultimately drove CRTs out of the market in 2007 (2010 in some parts of the world). Plasma displays with their better contrast ratio and darker blacks reached their peak around 2008, but succumbed to LCD displays in 2014 because of their potential screen burn-in issues [45.2] and the improved brightness and efficiency of LCDs [45.3]. Previous articles and books [45.4] have discussed these outdated technologies in more detail, so this chapter will focus on the current *battleground* technologies in modern displays, which are active matrix liquid crystal display (AMLCD) and OLED, as they continually push the boundaries on attainable resolutions, brightness, speed, and power consumption.

45.1.1 LCD Displays

To understand the requirements for the glass, we must first understand how these devices work. An LCD works by rotating the polarization of light to turn a pixel on and off, as illustrated in Fig. 45.1. Incoming light from a back light first passes through a polarizer on the outside surface of the LCD backplane substrate glass. On the inside of this glass is a thin layer of polymer with tiny grooves oriented parallel to the polarizer. The opposing parallel piece of glass called the color filter (CF) (the reason for this name will become apparent shortly) also has a grooved polymer layer on the inside aligned to a polarizer on the outside. However, the polarizers and grooves on the CF sheet are rotated 90° relative to the backplane sheet, so that the polarizers are crossed and no light should be able to get through. Now, if we fill the gap between the backplane and the CF with liquid crystal (LC), we can control the passage of light. The molecules of the nematic liquid crystal are long and polar. Thus, they align with the grooves on the inside surface of the backplane, then twist a little with each successive layer until they are rotated 90° and oriented with the grooves on the CF on the other side of the gap. Now, when polarized light enters the gap, it will rotate with the twisted nematic liquid crystal and pass through the polarizer on the CF, as shown on the left-hand side of Fig. 45.1. If a voltage is applied across the gap between the backplane and CF, the nematic liquid crystal molecules will orient parallel to the electric field and perpendicular to the glass sheets,

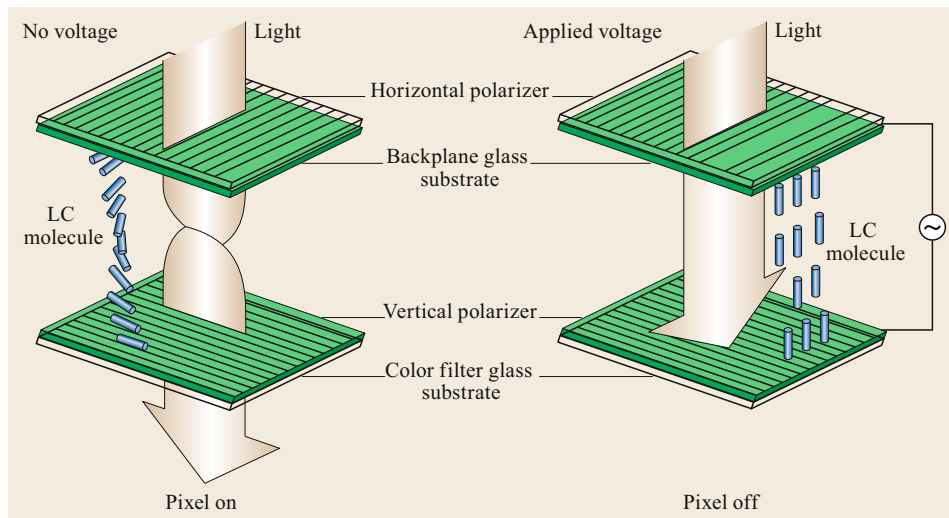


Fig. 45.1 Principle of LCD operation showing a bright pixel on the left and a dark pixel on the right

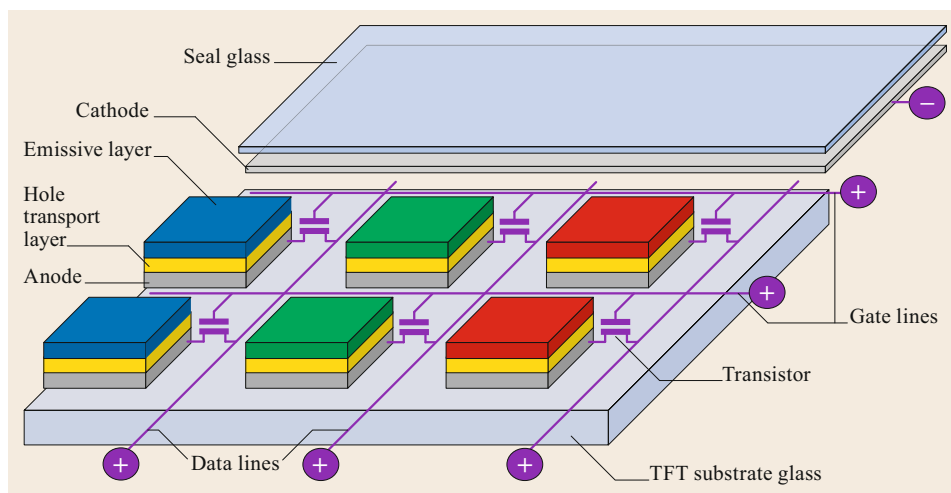


Fig. 45.3 Active matrix OLED display

be used in the horizontal gate lines for faster switching without impacting neighboring pixels and higher dynamic range of the display can be achieved, providing faster displays with greater contrast. However, these devices are more complex and require more than 6 million (1080 rows $\times$ 1920 columns $\times$ 3 colors) transistors and capacitors for a single 1080p HD TV with 1080 rows and 1920 columns, and more than 26.5 million transistors and capacitors for a 4 K TV with 4096 rows and 2160 columns; 8 K or UHD TV has 7680 rows and 4320 columns requiring 99.5 million transistors and capacitors to be built on a sheet of glass. Thus, there are tough demands on the glass substrate that must remain dimensionally stable during the fabrication process, since even 10 ppm of shrinkage or distortion would result in misregistration between the pixels in the backplane and those in the CF layers, which go through very different thermal processes.

45.1.3 AMOLED

Active matrix OLED (AMOLED) devices operate very differently than LCD devices, but as we will soon discover, have a lot in common with them. OLEDs work by emitting light directly, so they have a wider viewing angle, and there is no need for color filters, which absorb two thirds of the light, so they can be more efficient than LCDs. Even though linear polarizers are not necessary for optically switching OLED pixels on and off, they require a circular polarizer for ambient light rejection, so both LCDs and OLEDs lose half their light output via the circular polarizer. OLEDs also require a glass substrate on which to build the device and an array of conductors to address the transistors that switch the pixels on and off, as illustrated in Fig. 45.3. A transparent conductive oxide layer, usually ITO, is deposited as

the anode on the substrate. Then, an organic conductive layer is deposited to transport holes from the anode to the emissive layer. The organic emissive layer controls the color of the pixel, and red, green, and blue emitting organic layers are patterned as subpixels directly on top of the hole transport (injection) layer. The emissive layers are then contacted with a common cathode, usually with a low work function metal like Ca, to inject electrons into the emissive layer. The transistor controls the current flowing through the emissive layer, where the electrons and holes recombine to emit light with nearly 20% efficiency for red and green diodes but only 5% for blue diodes. The light emission is proportional to the current, so darker areas use only 40% of the power of an LCD, but white areas can consume three times the power of an LCD. The light is emitted in all directions, but in the case of a metallic cathode, it will reflect the light back out through the substrate. Nearly transparent displays can also be made with OLED devices with transparent cathodes. OLED displays also put high demands on the glass substrates. The low work function cathodes will oxidize if exposed to oxygen, and the emitting layers are degraded by exposure to water vapor, so the glass substrate and superstrate (seal) must be hermetic and impervious to air and humidity. Since OLEDs are current driven devices, the transistors require high mobility Si in their TFT arrays, which means high process temperatures, so the glass needs to have excellent dimensional stability during processing and a very smooth surface, just like LCDs.

45.1.4 Quantum Dot Displays

Quantum-dot light-emitting diodes (QLEDs) are an emerging display type, which could be a serious threat for OLEDs. In fact, Samsung, the largest TV maker in

the world, says that it is focusing on QLED instead of OLED [45.5]. There are two architectures for QLEDs. In one scenario, the quantum dots are simply used as phosphors not diodes, and red and green emitting quantum dots replace the red and green color filters in the CF panel, and the blue color filter is left out. Now, when blue LEDs are used as the sole light source, the blue light travels unimpeded through the now missing blue filter and excites the red and green emitting QDs. The LC controls the intensity of each subpixel just like a conventional LCD. In the second architecture, the QDs function as electroluminescent diodes deposited in the clear aperture between the TFTs. This type of display is like an OLED display, where the organic LEDs and conductive layers are replaced with inorganic QDs. When the TFTs are turned on, they pass current through the QLED, and direct red, green, and blue emitting QDs are used to generate light at the pixel. This technology provides deep blacks and high contrast ratio, since the pixels in the off state are extremely black [45.6]. Regardless of the architecture, most QLEDs still rely on active matrix backplanes with TFTs for best performance, so the requirements of the glass are still the same as for AMLCD and AMOLED devices.

45.1.5 Active Matrix TFT Technology

Independent of the display type, active matrix displays offer faster response and better dynamic range than their passive matrix counterparts. Whether it is LCD, OLED, or QD, most active matrix display technologies use one of three primary TFT backplane technologies: amorphous silicon (a-Si), oxide TFT (often called IGZO, short for indium gallium zinc oxide), or low-temperature poly-silicon (LTPS). These different TFT technologies differ somewhat in their designs but are primarily distinguished based on the material used as the semiconductor layer. The most commonly employed technology is the a-Si TFT backplane due to its simplicity, scalability, and low cost compared to the other options. Generally, a-Si based devices utilize lower temperature processes (200–300 °C peak temperature) and are lower resolution displays. The scalability of the a-Si technology, however, makes it very suitable for large displays, which often have lower resolution and less demanding power requirements than mobile devices. Higher performance displays (such as in extremely high resolution televisions or higher end mobile devices) place more demand on the TFTs,

requiring higher mobility semiconductor layers. The LTPS process enables considerably higher electron mobility than a-Si based TFTs (up to 100 times higher), allowing TFTs to be smaller, which enables higher resolution, lower power consumption, or both. TFTs are not transparent and are, generally, hidden under the black matrix between pixels, so the smaller they are, the more area available for the clear aperture to let light through the pixel. The ratio between the light emitting area versus the total area of a pixel, including the black matrix and opaque electronics, is called the aperture ratio. Higher mobility Si enables higher aperture ratio, so either the pixels can be brighter or smaller with LTPS. If they are smaller, then more pixels can fit in the same area, and resolution is increased. While LTPS can clearly enable a better display, there are many downsides as well, such as the higher temperatures required (as high as 600–700 °C) to grow the Si semiconductors, increased complexity of manufacture, higher costs, and the difficulty in scaling to large display sizes. The third technology, oxide TFTs, has, therefore, been getting a lot of attention in recent years, since it offers the scalability of a-Si but with increased electron mobility (although not as high as LTPS), which could enable high resolution and large displays. Currently, oxide TFTs are used mostly in tablets and are just starting to migrate to TV. This technology strikes a balance between a-Si and LTPS and, it will be interesting to see how widely adopted it is in the future amongst the large panel manufacturers [45.7].

Today's touch screen devices have more than just two pieces of glass. Figure 45.4 compares the components used to make LCD and OLED touch screen devices. Both can utilize four sheets of glass, including a chemically strengthened cover glass that is more scratch and damage resistant than the display glasses to protect them from breakage. They also have a thin touch sensor with an array of transparent electrodes to sense the location of a user's finger or stylus. Most multitouch sensors use capacitive touch with rows of transparent electrodes on one side of the touch sensor and columns on the other, creating small capacitors at each crossing. When a user's finger(s) touches the cover glass, it changes the capacitance at the nearby crossing(s) of the rows and columns on the touch sensor and is detected as a touch [45.8]. Some new phones integrate the rows and columns of transparent touch electrodes directly on the cover glass (on-cell touch) or directly on the display glass (in-cell touch) to eliminate the extra touch sensor glass layer for a thinner device [45.9].

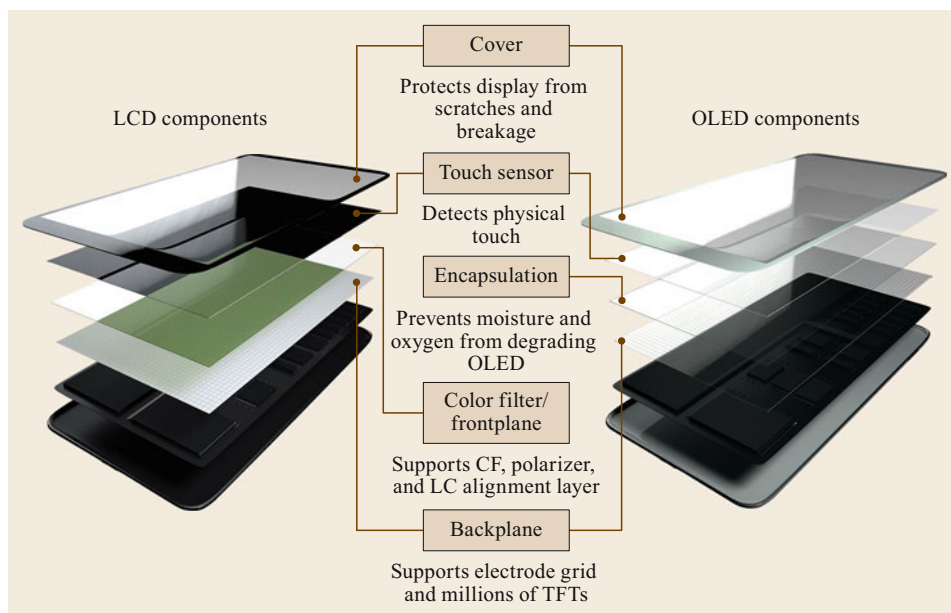


Fig. 45.4 Comparison of LCD and OLED touch screen components. Courtesy Corning Incorporated

45.2 Display Glass Properties

45.2.1 Basic Compositional Requirements

All glasses used in the industry today have to satisfy some basic requirements before they can be considered as display substrates. The first of these is to control alkali contamination, which can poison Si-based devices and cause performance issues in the TFTs. Most display glasses are considered *alkali-free*, although they all contain a low level (≈ 100 ppm or less) of alkali in practice from tramp contamination in the raw materials. This residual level of alkali is generally prevented from entering the TFT through the application of a barrier layer of silicon dioxide or silicon nitride on the substrate. Furthermore, the aluminum and boron ions in the glass have a strong affinity for alkalis and prevent them from diffusing out of the glass and into the Si [45.10]. So, while not truly alkali-free, a glass must have a low enough level of mobile alkali ions such that industry-accepted solutions to alkali-diffusion are effective.

Another historically pervasive attribute of display glasses is a low density. While not directly related to the performance of the device, a lower density glass would reduce the weight of the device (always critical in today's mobile devices) and would allow for easier handling of the large sheets in the manufacturing process. It also reduces sag during the manufacturing process. However, more recent glasses have seen their densities increase relative to the glasses used 10–20 years ago

as backplanes have become increasingly thinner while putting more stringent requirements on the total pitch variability of the substrates (this will be discussed in the next section). The fact that the substrates are thinned to only a couple of hundred μm in thickness means that the density of the glass contributes less weight to the overall device than previous designs. This lower contribution of weight to the article, therefore, reduces some of the value of a low density glass, allowing glass manufacturers to better optimize attributes that would improve display performance at the expense of increased density.

45.2.2 Total Pitch Variability

Within the display industry, there is an ever-increasing demand for higher resolution, brighter screens, or lower power consumption for longer battery life in mobile devices. To enable these improvements, perfect registration (or as perfect as possible) of the various layers of the TFT is critical. The TFT fabrication process can be simplified to a series of thin film deposition, photolithographic patterning, etching, and heat treatment steps. Just a few μm of shrinkage can cause a pattern error between successive photolithographic exposures if not properly compensated for [45.11]. Total pitch is the distance any given location or feature on a glass substrate moves during processing. If the shrinkage or total

pitch is uniform and reproducible from sheet to sheet, it is not a big problem. Reasonably large amounts of total pitch can actually be accounted for by compensation in the TFT process, traditionally up to 20–30 ppm. Since the TFTs and conductive paths are patterned photolithographically, the photo mask can be scaled up in size by 20–30 ppm, so that after processing, the product shrinks to the target dimensions and feature sizes and locations. If the total pitch is too large to be compensated for, considerable losses for the panel manufacturer due to dead pixels or light leakage due to misalignment of features (such as the TFT and color filter) would result. What is interesting is that, once below the upper limit of pitch change for a given process, further reduction in total pitch change does not necessarily lead to better alignment. Rather, improvements in variability of the total pitch (known in the industry as total pitch variation or TPV) will lead to better and more repeatable alignment. In other words, a larger but less variable total pitch value is preferred to a smaller but more variable value (although it should be noted that the ultimate desire is often minimal total pitch and minimal total pitch variability). This is due to the fact that, once a given amount of total pitch is identified for a given process, the optical compensation can take care of any change in total pitch as long as it is consistent and does not vary. A reduction in total pitch variability can increase the selects of a panel manufacturer's process, thereby improving their economics. Beyond cost savings, reducing total pitch variability can also allow the panel manufacturer to improve their aperture ratio. A higher aperture ratio would allow for more light to be emitted at a given resolution (enabling better battery life and/or brightness) or higher resolutions at a fixed aperture ratio. However the manufacturer chooses to *spend* the improved TPV performance of the substrate, the end result is a better and/or less expensive device. Therefore, total pitch variability has become the most

important distinguishing factor between potential substrate glasses.

Translated to glass properties, this means the glass backplane must demonstrate the minimal amount of total pitch variability possible. Historically, this was described by the *compaction* or *shrinkage* performance of the glass, which is the dimensional change undergone by the glass under a thermal cycle in the manufacture of the TFT, often at the highest temperatures in the process like the dehydrogenation step in a LTPS process. The bulk of this dimensional change is due to viscous relaxation, which can also be described as the relaxation of the fictive temperature of the glass (defined as the temperature corresponding to the equilibrium state described by the structure trapped in the glass during formation) towards the temperature of the display panel maker's process. This became known as *compaction* due to the fact that the fictive temperature set into the glass during manufacture is often above the heat treatment temperature of the glass during the TFT process. Unlike crystalline materials, the density of a glass is dependent on thermal history and can change with heat treatment. If the heat treatment temperature is below the fictive temperature of the glass, relaxation of the glass structure during processing will result in a reduction of fictive temperature, as shown in Fig. 45.5a. A lower fictive temperature glass has a more dense structure and will, therefore, occupy a smaller volume, resulting in compaction or shrinkage of the glass during the heat treatment. Unlike crystalline materials, the final volume and density of glass is dependent on the thermal history of the glass. Figure 45.5b shows the change in volume as it is cooled at different rates. At high temperatures, the glass has a low viscosity, and the structure relaxes quickly and the volume contracts independently of the cooling rate, hence the two curves are coincident at high temperature. However, as the glass becomes more viscous at lower temperatures, the struc-

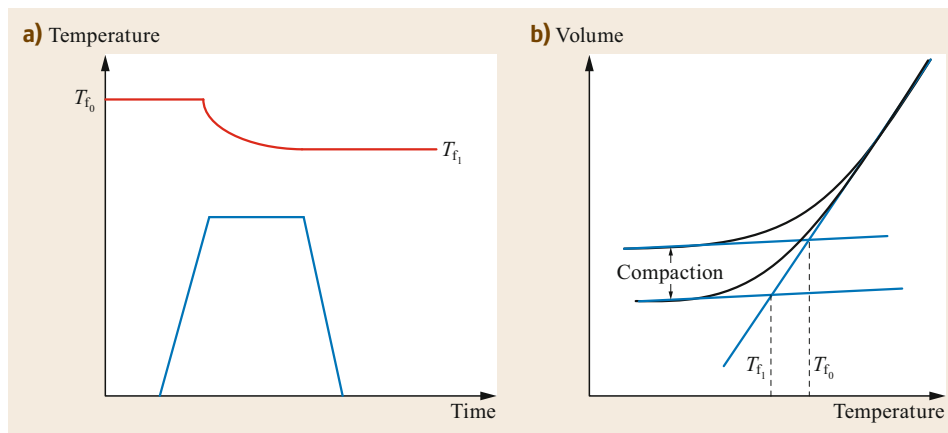


Fig. 45.5a,b
Change in fictive temperature with
(a) time and
(b) temperature

ture cannot equilibrate quickly enough to keep up, and the volume contraction will slow down and follow the upper curve and transition from the volume contraction curve of the liquid melt at high temperatures to the volume contraction of the solid glass at low temperatures and set in a fictive temperature of T_{f0} . If the glass is cooled more slowly, the glass has more time to relax and can equilibrate at higher viscosities (lower temperatures) and contract to a denser lower volume state as illustrated by the lower curve and have a lower fictive temperature T_{f1} . In practicality, most glasses will lock in a fictive temperature corresponding to a viscosity of between the strain point ($10^{13.7}$ Pa s) for extremely well-annealed optical glasses and 10^{10} Pa s for fusion drawn glasses. When heat treatments are made to the glass after forming, its fictive temperature will relax towards the heat treatment temperature. If the heat treatment temperature is below the fictive temperature, the glass will contract, and the lower the temperature, the slower the rate of equilibration and densification. If the heat treatment temperature were instead above the fictive temperature of the glass, the fictive temperature would increase during relaxation, causing an expansion of the glass. It is, therefore, more proper to refer to this phenomenon as *dimensional change* rather than *compaction*, since the latter is shaded by empirical experience in the industry and is not reflective of the actual physics in play.

While the total pitch of a substrate was historically attributed to the structural relaxation of the glass due to these changes in fictive temperature, total pitch is actually due to a number of factors and not just the change of the average fictive temperature of the glass. In the following sections, we will discuss some of the most important of these factors, each of which have an additive contribution to the TPV:

1. Elastic distortion
2. Stress relaxation
3. Viscous relaxation.

Elastic Distortion

Perhaps the easiest to understand of the factors contributing to total pitch variation is elastic distortion. During the manufacture of a TFT, various films are deposited on the glass. While efforts are made to minimize stresses in these films, invariably there is residual stress in the films, which then causes a concomitant strain in the glass. The resulting pitch change in the substrate is consequently governed by the elastic modulus of the glass E and the thickness of the substrate h , as seen in the Stoney equation

$$\sigma_f t_f = \frac{E h^2}{6(1 - \nu)R} \quad (45.1)$$

In (45.1), σ_f is the in-plane stress in the film, t_f is the film thickness, E is the Young's modulus of the substrate, h is the thickness of the substrate, ν is the Poisson's ratio of the substrate, and R is the radius of curvature of the substrate after the film deposition [45.12]. When there is no film stress, $\sigma_f = 0$, R must go to infinity, and the sheet is perfectly flat. As can be seen from the equation, when a higher stress film (or thicker film) is applied to a glass substrate with a given modulus and thickness, the radius of the curvature must decrease, resulting in decreased R , and increased warp. Similarly, for a given film stress and film thickness, an increase in either the Young's modulus or the substrate thickness will result in an increase in the radius of curvature of the substrate, resulting in less warp and a flatter sheet. While the most efficient way to reduce distortion due to film stresses is by increasing the thickness of the substrate (varies as thickness squared), the display industry is constantly driving to thinner and thinner substrates. Consequently, a higher modulus glass is one of the only ways one can reduce the pitch change from a given applied stress from the films, thereby reducing the contribution to total pitch from elastic distortion. Similarly, variations in applied film stress will cause variations in the resulting strain in the glass, so a glass with a higher Young's modulus would also reduce the TPV due to elastic distortion.

Stress Relaxation

Once films with stresses have been applied to the glass substrate during TFT manufacturing (often during the early steps of the process), subsequent time spent at elevated temperatures can result in the relaxation of both the film and the glass. This can be a source of TPV if the sheet experiences different temperatures during later steps in the manufacturing process or if there are variations in initial film stress, causing varying degrees of relaxation.

This stress relaxation happens much faster (roughly $10\times$) [45.13] than the bulk structural relaxation corresponding to the evolution of the fictive temperature of the glass during heat treatments (covered earlier and in the next section) and can, therefore, be a major source of dimensional change in the glass at lower temperatures where bulk structural relaxation has a negligible contribution to dimensional changes. The rate of stress relaxation is governed primarily by the viscosity of the glass at the processing temperature. In fact, the measurement of stress relaxation in a controlled lab environment can be used as a way to directly measure the non-equilibrium viscosity of a glass at an experimental temperature.

At high temperatures (well above the glass transition temperature), the glass structure is in virtually instant

equilibrium with any perturbations to temperature. Consequently, the viscosity–temperature relation of a glass at high temperatures can be easily described by a smooth function. At lower temperatures, however, the viscosity of the glass is much more complicated. This low temperature viscosity is not only a function of the composition of the glass (which determines the viscosity–temperature curve) and the temperature of measurement but also of the thermal history of the glass and time. As a glass is cooled through the glass transition region, the structure ceases to evolve and is frozen at the fictive temperature. When the structure ceases to evolve, the viscosity of the glass departs from the smooth equilibrium viscosity curve and begins to follow a different trend with an effective viscosity (solid line in Fig. 45.6) below that which would be predicted exclusively from the equilibrium curve (dashed line in Fig. 45.6). This lower viscosity is due to the more open structure trapped in the glass characteristic of its higher fictive temperature. The degree of the departure of the glass from the extrapolated equilibrium viscosity curve is, further, dependent on the fictive temperature of the glass (and, therefore, on the cooling rate of the glass) with a higher fictive temperature glass having a lower viscosity than the same composition with a lower fictive temperature. Because of this, maximizing the viscosity of a glass through composition design, thermal history manipulation, or a combination of both, is the best way to reduce the amount of stress relaxation a glass undergoes during TFT manufacturing. Assuming a similar thermal history, the amount of stress relaxed in a given time at temperature should scale directly with the annealing point of the glass (which is a good metric for low temperature viscosity as it is the

temperature where the glass viscosity is $10^{12.2}$ Pa s). To measure stress relaxation, a load is applied to a beam of glass at temperature to induce a specified amount of deflection. The stress relaxation is then calculated from the decay in the force required to maintain the specified deflection. In Fig. 45.7, several glasses with varying annealing points are held at relevant temperatures for TFT processing, and the expected trend is precisely what is observed—the higher the annealing point of the glass, the less stress relaxation. The less stress relaxation, the lower the TPV, so higher annealing point glasses are desirable for reducing stress relaxation.

Viscous Relaxation

Also referred to as structural relaxation, viscous relaxation of a glass is governed by the relaxation of the non-equilibrium nature of the structure of a glass towards the structure consistent with the temperature of the process step at hand due to changes in fictive temperature. The time dependence of viscous relaxation is roughly described by the Kohlrausch–Williams–Watts (KWW) equation [45.14]

$$T_f(t) = T + [T_f(t=0) - T]e^{-\frac{t}{\tau(T, T_f)}}, \quad (45.2)$$

where $T_f(t)$ is the change in fictive temperature as a function of time, T is the temperature of the thermal cycle in question, $T_f(t=0)$ is the initial fictive temperature, and $\tau(T, T_f)$ is the relaxation time, which is proportional to the viscosity of the glass with said fictive temperature at the temperature of the thermal cycle. In simplistic terms, the rate of this relaxation depends on the driving force for the dimensional change and a re-

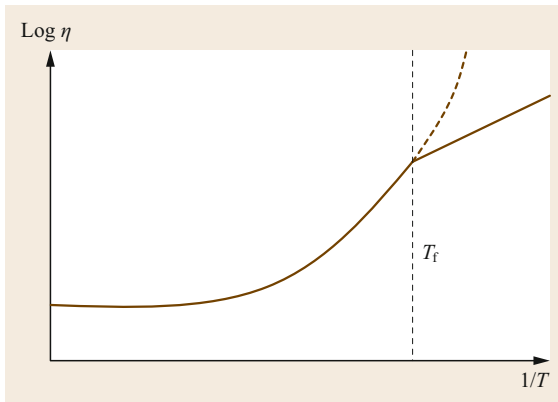


Fig. 45.6 Equilibrium and non-equilibrium viscosity. Below T_f , the glass structure is locked in, and the effective viscosity (*non-equilibrium viscosity*) becomes lower than the theoretical viscosity the glass could have if it were allowed to fully equilibrate at a given temperature (illustrated with the *dashed line*)

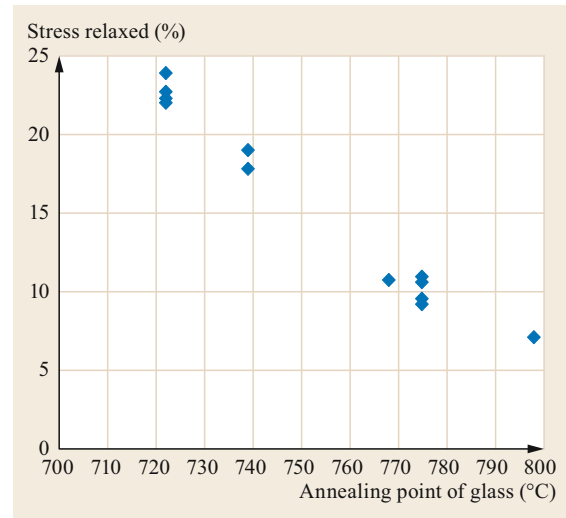


Fig. 45.7 Stress relaxation as a function of glass annealing point

sistance to that change. The driving force in this case is the deviation of the fictive temperature of the glass from the temperature of the process step . . . the larger the deviation, the larger the driving force for structural relaxation. The resistance to this change is the exponential term in (45.2) and is proportional to the effective viscosity of the glass, which is a function of the glass composition, its fictive temperature, and the temperature of the process step (as discussed in Sect. 45.2.2, *Stress Relaxation*). A reduction in the amount of dimensional change due to structural relaxation can be achieved by either reducing the driving force or increasing the resistance to the change. Reducing the driving force for dimensional change can be accomplished by reducing the difference between the fictive temperature of the glass and the temperature of the heat treatment step. This is illustrated in Fig. 45.8 in the comparison of the standard glass with the same glass that has been annealed at the heat treatment temperature for some time. This plot in Fig. 45.8 shows the dimensional change as a function of time at temperature up to 120 min. While the *low viscosity* glass immediately compacts even at the shortest times, the annealed version does not start showing appreciable compaction until it has been held at temperature for over 15 min. Even at long times, the annealed glass continues to demonstrate considerably reduced dimensional change relative to the composition with the higher fictive temperature. Alternatively, increasing the resistance to a change in fictive temperature can achieve a similar result. In the right image, a higher viscosity glass is compared to the same standard glass as used in

the annealing study. This glass also has minimal dimensional change until it has been at temperature of over 15 min and ends up at virtually the same level of dimensional change as the annealed sample, demonstrating the similar efficacy of both approaches.

Since annealing or extremely slow cooling a glass can be cost prohibitive, a very attractive way to reduce the dimensional change observed in a given thermal cycle is to maximize the low temperature viscosity of the glass. As can be seen in Fig. 45.9, if an equivalent cooling rate is applied to a series of glasses with increasing annealing point, the compaction continuously decreases in a high temperature test cycle. This strong correlation of the low temperature viscosity of the glass (i.e., the annealing point) with reduced dimensional change is one of the key factors driving the historical increase in the annealing point of display substrates. Furthermore, the temperatures used by display panel manufacturers are not always known and can vary from one manufacturer to another and can even change when different products are being made, so overcoming dimensional change with increasing viscosity is a more robust solution than annealing the glass.

45.2.3 Physical Requirements

While we have discussed a number of compositional requirements for a display glass, the physical requirements for use as a display glass are every bit as stringent. The glass must be exceptionally flat, have low stress, and be clean. The TFT performance can

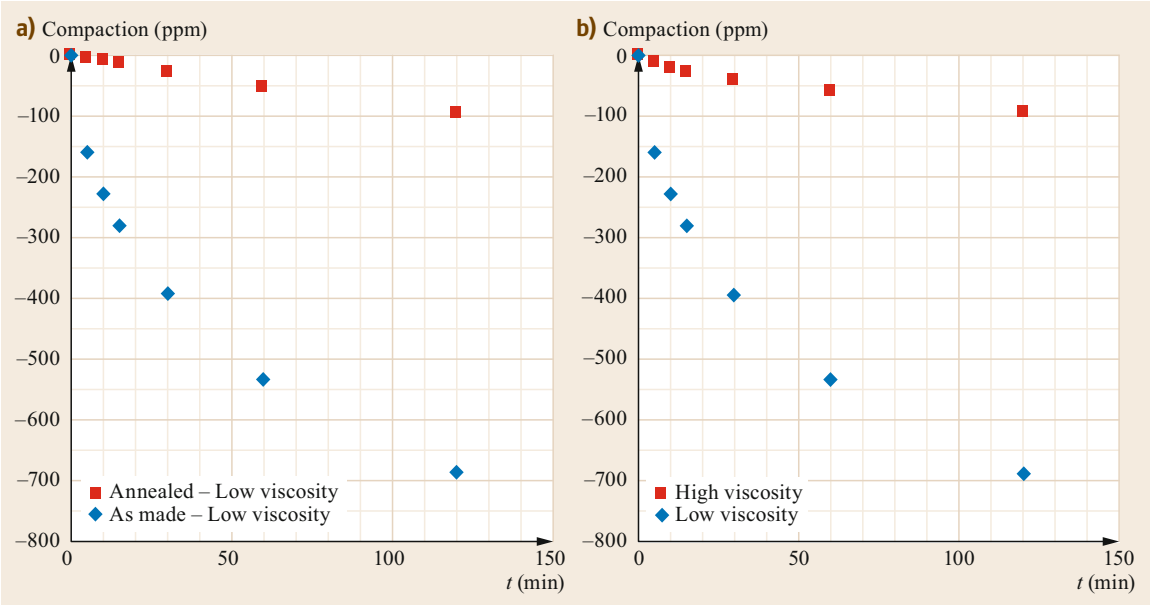


Fig. 45.8a,b Dimensional change (compaction) as a function of time for (a) annealed (squares) and as formed (diamonds) glass and (b) low (diamonds) and high (squares) viscosity glasses

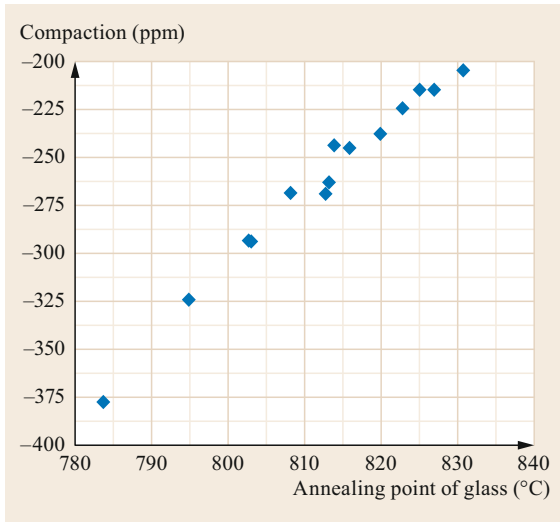


Fig. 45.9 Compaction as a function of the glass annealing point

45.3 Melting and Fining

Melting is the process of dissolving solid batch materials into a liquid melt, while fining is the process of removing gaseous inclusions or bubbles from the melt. Display glasses need to not only survive the high temperature TFT manufacturing process, but the sheet must remain dimensionally stable so that it does not warp or shrink to maintain pixel alignment between the TFT and CF panels, which requires a high annealing point, as discussed in Sect. 45.2.2. Unfortunately, raising the annealing temperature of the glass also makes it harder to melt and remove bubbles. Figure 45.10 compares the viscosity curves of display glasses to typical soda-lime silicate. The display compositions are roughly 200–300 °C higher in annealing point with a commen-

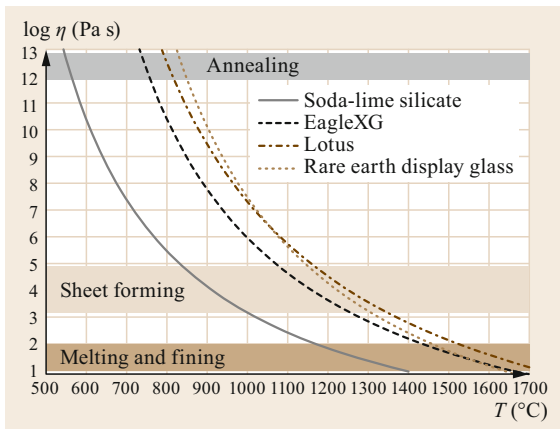


Fig. 45.10 Viscosity curves of exemplary glasses

be detrimentally impacted if the surface has too much roughness (from scratches or even just the general surface texture). Similarly, a glass substrate with too much distortion or shape can cause handling errors in coarse scale or cell gap deviations in smaller scales. The cleanliness of the substrate must be exceptional, with particles on the order of $< 1 \mu\text{m}$ causing visual defects in the resulting display. In high performance displays, the monitored particles may be as low as $0.3 \mu\text{m}$ in diameter. If not carefully monitored, particles can cause massive losses in the manufacturing process (as was the case in the early days of AMLCD manufacture). Thus, the glass needs to be transparent, extremely flat, thermally stable, clean, and chemically stable. To achieve these attributes, the glass composition needs to melt well, have a high liquidus viscosity and annealing point while being compatible with a forming process that is capable of making flat precision sheets. The melting and forming processes used to achieve these feats will be explored next.

surate increase in the temperatures required to lower the viscosity of the melt to between 10 and 100 Pa s, where the batch materials quickly dissolve and trapped gas bubbles can rise to the surface in a reasonable amount of time.

45.3.1 Melting

When batch enters the melting tank, fluxes such as boric acid and alkaline earth carbonates decompose to oxides and react with some alumina and silica to form fluid melts. These melts become enriched with more alumina and silica as the melting progresses causing the viscosity to increase. To make pristine glass and eliminate solid inclusions such as unmelted batch, the batch must be fully dissolved into the melt before the glass begins to cool. The rate of dissolution of any solid particle will be determined by the solubility of the particle in the surrounding glass melt and the diffusivity of the component ions of the particle in the glass. The solubility is determined by the identity of the particle and the composition and temperature of the glass melt. The diffusivity D is inversely proportional to viscosity as described by the Stokes–Einstein equation [45.15]

$$D = \frac{k_B T}{6\eta\pi r_H}, \quad (45.3)$$

where $k_B = 1.38 \times 10^{-23} \text{ J/K}$ is Boltzmann's constant, T is the absolute temperature, η is the viscosity, and r_H is the hydrodynamic radius of the ion [45.16]. Thus, increasing temperature will increase T and decrease η ,

which will both increase D , as well as the solubility of the particle components, and combined they greatly increase the dissolution rate of any remaining sand grains or other batch materials. However, the glass melting tank walls are made of ceramic refractories similar to the batch materials (primarily SiO_2 , Al_2O_3 , and ZrO_2), so increases in temperature will increase the rate of tank corrosion and shorten the usable tank life, causing costly down time and tank rebuilds. In fact, the tank corrosion rate roughly doubles for every 50–100 °C increase in temperature [45.17]. Thus, there must be a balance between the glass melting rate and the tank corrosion rate. For example, very high SiO_2 (> 94%) glasses with annealing points greater than 1000 °C have long been known [45.18], but they are not economically feasible to melt and must be made by more expensive, lower throughput means. Alkali metal oxides like Li_2O , Na_2O , and K_2O are extremely effective for dissolving SiO_2 grains because of their high diffusivity and viscosity lowering power, which improves melting and fining. Hence, they are used in most glasses for windows and containers, but they are forbidden in display glasses because their high mobility quickly poisons Si transistors. Thus, display glasses are considerably more challenging to melt than their alkali-containing counterparts and require higher temperatures and more advanced tank materials. Higher annealing point glasses needed for improved display glass performance also increase the viscosity at melting temperatures, making them even more difficult to melt and fine. Thus, the glass composition should be designed to have a steep viscosity curve, so that it has a high annealing point for good TPV performance and yet a reasonable melting temperature and high batch dissolution rate to enable efficient production of high quality glass. The dissolution rate can also be improved by judicious selection of raw materials and their particle size.

45.3.2 Fining

The melting of typical display glass raw materials produces a lot of gas. Alkaline earth carbonates release CO_2 , while the trace amounts of nitrates and sulfates liberate N_2 , O_2 , NO_x , and SO_2 . There is also a considerable amount of air trapped between melting batch particles, which then expands with increasing temperature and further increases the gas load in the molten glass. Bubbles are lighter than molten glass, so they float to the top at a rate that is determined by the viscosity of the surrounding glass melt [45.19]. The upward terminal velocity v of a bubble of radius r in a glass melt of viscosity η , and density ρ is given by

$$v = \frac{2gr^2\rho}{9\eta}, \quad (45.4)$$

where g is the acceleration due to gravity [45.20]. While larger bubbles rise fast enough to be eliminated quickly, the smaller bubbles are the most troublesome, since they are impeded by the viscous drag. To observe this speed differential at room temperature, just vigorously shake a half empty bottle of a viscous liquid like liquid soap and watch the large bubbles race past the tiny ones on their ascent. A 0.1 mm diameter bubble will only rise about 10 cm/day in a glass melt of 10 Pa s viscosity, which is far too slow for effective removal. The temperature of the glass can be increased to reduce the viscosity, but the slope of the viscosity curve is relatively shallow in the melting and fining regime of the viscosity curve shown in Fig. 45.10, so lowering the viscosity by a factor of 100 to 0.1 Pa s would require a 400 °C increase to well above 2000 °C, which is far beyond the capability of any large scale melter and the materials used to contain the molten glass. However, the upward velocity is proportional to r^2 , so if the size of the bubble could be increased by 10 $\times$, then a 1 mm bubble will rise 100 $\times$ faster according to (45.4). So, ironically, the key to fining is to generate more gas and make small bubbles larger, so they can be removed quickly [45.19]. As_2O_5 is a very powerful fining agent and has been used for centuries, since it tends to reduce at high temperatures (liberating oxygen) and then oxidize at low temperatures according to (45.5) [45.21, 22].



To generate a new bubble requires the generation of a new gas–liquid interface creating a nucleation barrier to generating new bubbles. Furthermore, the capillary pressure inside a bubble is inversely proportional to the radius of the bubble, so it takes a lot of pressure to nucleate a tiny bubble. Thus, it is energetically more favorable for the O_2 generated by the As_2O_5 reduction to preferentially go into existing bubbles during fining, rather than generating new bubbles. So, once the glass is melted and the large bubbles have already risen to the top, the glass laden with residual tiny bubbles (or seeds, as they are called in the glass industry) then enters the fining section of the melter, where the temperature is increased, causing a reduction of the fining agent and the liberation of O_2 , which makes the small bubbles larger and increases their upward velocity. The glass depth is also typically shallower in the fining section, so the bubbles have less distance to rise to the surface. As the glass is conditioned in the sections after the finer and cooled for forming, any residual small O_2 bubbles will then be resorbed as the As_2O_3 is oxidized back to As_2O_5 . Since increasing temperature drives (45.5) to the right, decreasing temperature will drive it back to the left and aid O_2 resorption as the glass cools. As the temperature decreases, so does the volume of gas (according to the

ideal gas law $PV = nRT$). Hence, the bubble shrinks, which increases the surface area to volume ratio of the bubble and the capillary pressure inside, both of which aid in the reversal rate of (45.5). As_2O_5 is ideal for chemical fining because there is a large shift in the redox ratio at typical glass melting temperatures, and it has a large solubility in most glasses. Unfortunately, As_2O_5 is toxic and now highly regulated; SnO_2 is a safe non-toxic multivalent oxide also capable of chemical fining via (45.6) [45.19].



Unfortunately, SnO_2 is not as soluble as As_2O_5 in most glasses of interest, so its concentration is limited to a few tenths of a weight percent, which limits the amount of chemical fining. At high SnO_2 concentrations, the liquidus temperature increases and crystalline SnO_2 (cassiterite) will precipitate, decreasing the liquidus viscosity of the glass limiting the forming options available. To make matters worse, typically only a few percent of the total SnO_2 reduces to SnO at typical fining temperatures, further limiting its fining capacity, unlike As_2O_5 , which exhibits almost an order of magnitude greater redox change and works over a much wider temperature range. In fact, if 1 wt% As_2O_5 in the glass is replaced with 0.25 wt% SnO_2 (near the solubility limit for some display compositions) in lab melts, the bubble concentration increases by orders of magnitude. Thus, the melting process, raw materials, and

redox state of the glass need to be tuned and more carefully controlled to eliminate bubbles with SnO_2 [45.19]. Nitrates are also added to make the initial melt as oxidized as possible for maximum oxygen capacity.

To evaluate the effect of composition, batch materials, time, and temperature, 1 kg batch size crucible melts can be melted with an accelerated schedule to exacerbate the bubble problem and amplify the differences between different materials and melt conditions. Figure 45.11 shows the bubbles in cross-sections of intentionally under-melted glasses. The samples were cored from a glass melted in a 600 cm³ Pt crucible at 1500 °C for 1 h followed by 1 h at 1600 °C. This mimics fining in a tank, but with shorter times and temperatures to elevate the bubble signal. The first glass is the control sample with no fining agent and shows thousands of bubbles. SnO_2 fining agent was added to the second and improved, but still has hundreds of bubbles remaining. Tuning the raw materials and the base glass composition further improves fining, as shown in the middle and center right images in Fig. 45.11, although it was still unacceptable. Finally by tuning the process temperature to the new composition, the bubbles were eliminated and the high quality sample on the far right was obtained. Thus the glass composition, batch materials, fining agent, process, and melting equipment must all be optimized in concert to achieve high quality molten glass. Next, the processes to turn this high quality melt into high quality sheets will be explored.

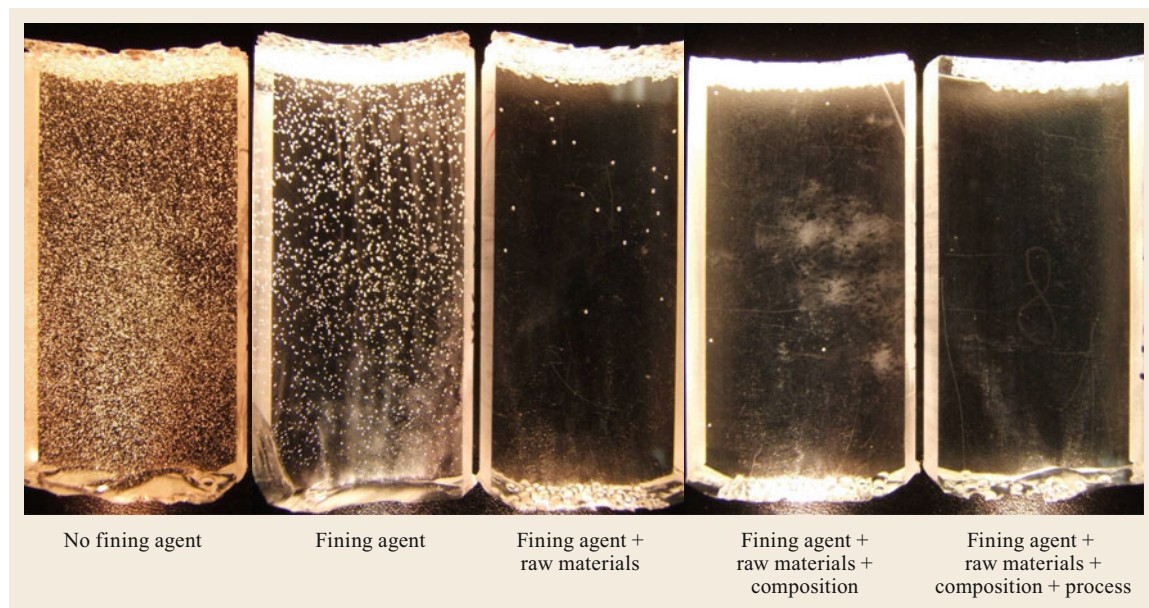


Fig. 45.11 Polished cross-sections of glasses melted at 1500 °C for 1 h followed by 1 h at 1600 °C revealing the fining performance. From [45.19]

45.4 Forming Precision Sheets for Displays

Glass substrates for LCD and OLED displays must be very flat, smooth, and dimensionally stable, and then remain that way through the various high temperature processing steps required to make displays. The surfaces must be pristine, flat, and smooth, since the layers of the TFTs grown on them are only nanometers thick, so any protrusions or roughness that may penetrate these layers would result in a dead pixel. Additionally, the gap between the back plane and color filter layer is only a few μm wide, so any warp or surface inhomogeneities would change the gap and, hence, the thickness of the liquid crystal layer between them and either kill the pixels near the defect or decrease the contrast and brightness of the display near the defect. Furthermore, many devices are made on a single sheet of glass, so large sheets are necessary for economies of scale. Thus, we need a forming process capable of making large precision sheets with extremely flat, smooth, and clean surfaces with high throughput and low cost.

45.4.1 The Slot Draw Process

Making flat sheets of optical quality glass is nothing new. Glass makers have been struggling for thousands of years to make optical quality windows ever since the Egyptians first discovered glass and the ability to plastically form it while hot. The methods evolved from the crown process of rapidly spinning a hot gob of glass on the end of a ponty to the cylinder process of up drawing a large hollow cylinder of glass, slicing it longitudinally, and opening up the cylinder and sagging it to a flat sheet. The first method suffered from radial thickness gradients and the latter from a poor surface after sagging. These were followed by the Fourcault process [45.23] of up drawing glass through a floating refractory slot to form a sheet, but corrosion of the refractory slot led to long threads of corrosion products and optical distortion of the surface [45.24]. Colburn improved the Fourcault process by taking the glass from the free surface of the glass melt and pulled it upwards using knurled drive wheels to stabilize the edge of the sheet and prevent surface tension from collapsing the width of the sheet and drive it upwards. Colburn also reheated the glass just above the up draw and bent it 90° over a polished roller to turn it horizontally and feed directly into a lehr [45.25]. Sadly, neither Fourcault nor Colburn lived long enough to see their processes achieve commercial success [45.24], but by the mid 1900s the world's production of sheet glass was roughly 72% Fourcault, 20% Colburn, and 8% some combination of the two [45.26].

Don Brown at Corning Incorporated turned the up draw process upside down and designed a clever slot that extended downwards along the edges at 30° , as shown in Fig. 45.12 to make thin, uniform thickness sheets without any edge beads in the early 1940s. Surface tension of the glass ribbon acts to reduce the width of the drawn sheet, but the angled slot on the edges provides an outward lateral force from the surface tension of the glass on the lowest vertical portions of the slot, and the slot also provides additional glass flow near the edge and at a lower vertical location, so the sheet is wider than what would be achieved with a simple horizontal slot. The precision slot orifice is typically made of a refractory metal like Pt, so that corrosion and wear do not degrade slot geometry nor contribute to cord or solid inclusions on the surface of the sheet as a refractory oxide would [45.27]. The slot process was used to produce a range of very thin microscope cover slips around $100\mu\text{m}$ thick from Corning 0211 glass and 30 years later thicker sheet was sold as Corning's first LCD product when LCD technology

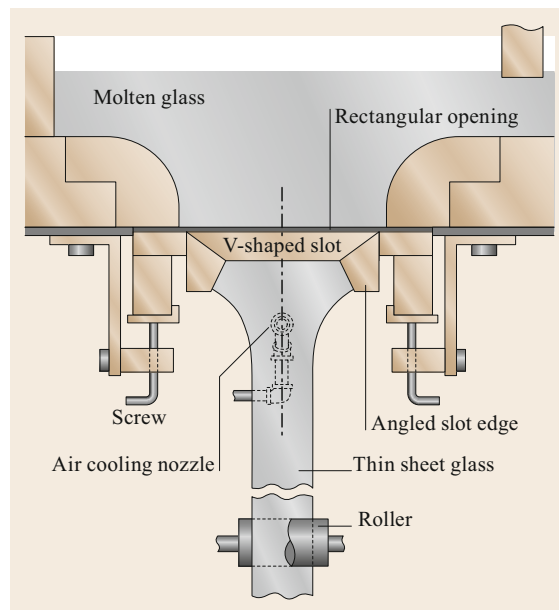


Fig. 45.12 The slot draw process. Molten glass is contained by a refractory melting tank with a rectangular opening in the bottom, which has the slot die consisting of the V-shaped slot and angled slot edges. This die is clamped to the bottom of the glass tank by screws. The molten glass emerges through the die as a sheet, which is then cooled by air blown through the nozzle to form a thin sheet, which is pulled by rollers to control the sheet thickness and apply tension to keep the sheet flat (after [45.26])

emerged in the 1980s. The slot drawn surface is a very smooth fire polished surface and was well suited for early displays, which were quite small (watches, calculators, indicators, etc.). However, the large scale warp was not suitable for today's larger devices and devitrification and the slot orifice shape had to be carefully controlled to avoid thickness bands and changes in the sheet geometry. Nevertheless, modern control systems can alleviate many of these early challenges [45.21], and, in fact, Schott Glass used a variant of the slot draw method to make very thin LCD glass for mobile applications [45.28].

45.4.2 Float

Even though several of the main features of the float process were patented by *Henry Bessemer* in 1848 [45.29], the float glass process was not successful in producing saleable glass until refinements were made by *Alastair Pilkington* [45.30] a century later. After the first full-sized float line was built in 1957, it took 7 years of problem solving, development, and patient investment (£7 million in 1960 or \$200 million in today's dollars) by Pilkington Brothers Ltd. [45.31] until the process finally became profitable and quickly made all previous methods of making flat glass obsolete [45.24]. In the float process, glass is delivered onto a bath of molten tin at a viscosity of about 1000 Pa s, as shown in Fig. 45.13. Since the glass is less dense than the molten tin, it floats on top. Gravity naturally makes the surface of the molten tin flat, which in turn makes the molten glass flat on both the top and bottom sides. The glass is held on the molten tin long enough (about 1 min) at a low enough viscosity (1000 Pa s) to even out any surface irregularities and for the surfaces to become flat and parallel. The tin bath is in a controlled atmosphere to prevent oxidation of the metal and is also in a thermal gradient so that the glass cools and stiffens as it moves across the molten tin before it is pulled off the cooler end of the bath by rollers at roughly 10^{10} Pa s. The balance of surface tension and gravity produces an equilibrium thickness of

6–7 mm, depending on the density and surface tension of the glass, but thicker and thinner sheets can be produced by side walls and stretching, respectively. The process was improved by delivering the glass to the tin bath over a wide refractory lip just above the tin bath to prevent the aggressive corrosion that takes place at the glass/tin/refractory triple point and reduce cord (Fig. 45.13). This design also moved the refractory-laden glass layer previously in contact with the lip to the interior of the sheet, so that any corrosion products from the refractory lip were encapsulated deep within the glass rather than on the surface, which prevented surface devitrification and optical disturbances that had previously plagued the bottom side of the sheet [45.31]. The relatively slow cooling on the long float process line anneals the glass and lowers its fictive temperature, so the float process produces glasses with relatively low compaction for its annealing point. The float process is used to make the vast majority of all flat glass produced worldwide because it is able to provide enormous volumes of large format soda-lime window quality glass at low cost. While float glass is perfectly suitable for windows, the float-formed surface is rougher than the competing processes for display substrates and must be ground and polished before use. The high temperatures required to float alkali-free display compositions cause evaporation and degradation of the tin bath, which is challenging to manage. Thus, float glass is just a small fraction of the glass used for displays. However, Schott pioneered the use of microfloat technology, which is, as the name implies, much smaller than traditional float processes. This reduction in size allows process innovations to be implemented that enable much higher process temperatures than the traditional float process. By reaching higher melting and forming temperatures, microfloat is able to produce higher strain point glasses than soda-lime and also in the smaller volumes and thinner formats required for display glasses. Pilkington and Saint Gobain also used the microfloat process [45.32]. *Asahi Glass Company* produces its AN100 AMLCD substrate product launched in 1998 using the microfloat process [45.33].

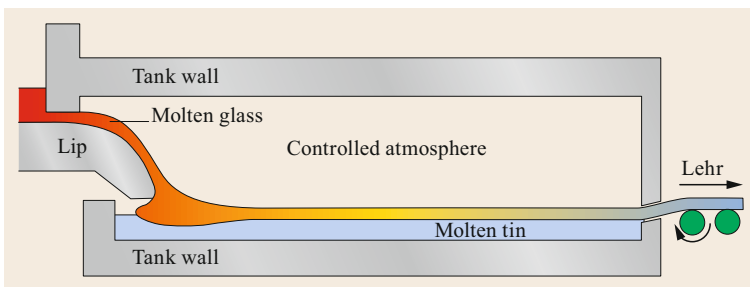


Fig. 45.13 Cross-section of the float glass process

45.4.3 Fusion

While a floated glass surface is perfectly suitable for windows and windshields, the surface is still too rough and wavy for LCDs and must be polished, which increases cost [45.34]. Shortly before float glass took over the windshield market in the 1960s, Corning engineers Stuart Dockerty and Clint Shay began working on a forming process in which both sides of the glass were untouched and pristine for automobile windshields. Windshields required better quality glass than the ordinary windows available at the time to avoid distortion and improve safety. They realized that the forming mandrel or tool had to be inside the glass to achieve this feat. They began with a tube with a tear drop shaped cross-section and put a slot in the top of the tube rather than the bottom. Incoming glass would fill the horizontal tube to the top and then overflow both sides of the tube at the top, run down both sides and then fuse back together at the sharp point of the downwardly converging sides. This fusing of the two sheets running down both sides of the pipe buried the refractory contact surface in the middle of the sheet, leaving both surfaces untouched and pristine [45.35]. Dockerty then modified the tube into a wedge shaped V with a trough on the top, as shown in Fig. 45.14. This knife shaped forming mandrel was designed to create a uniform rate of glass flow over the trough walls along the entire length of the tube or pipe and became known as an isopipe. Once the flow from both sides of the isopipe fused together at the bottom or root of the isopipe, gravity pulled the sheet straight down, assisted by knurled edge rolls to maintain the width of the sheet. The sheet cools as it travels downward and sets into a rigid solid where pulling rolls control the downward speed of the sheet. The sheet thickness is controlled by the speed of these rolls and sheets < 0.1 to 10 mm thick can be made by this process.

The fusion process has several advantages. First the surface is impeccable and flat, any contamination from dissolution of the isopipe is buried in the middle, where it would not disturb the untouched outer surfaces, which have been naturally flattened and polished by the surface tension. Today's fusion surface has a root mean square (RMS) roughness of less than 0.5 nm [45.11], which is most impressive considering SiO_4 tetrahedra (the fundamental building block of a silicate glass) are about 0.26 nm on a side! Second, inevitable wear of the isopipe will not distort the flow, shape, or thickness of the sheet. In slot processes like the Fourcault, Coburn, or slot draw processes, the sheet thickness will change as a function of the slot width. In the slot draw process, the width of the slot meters the flow of glass, so as the slot widens, flow increases, and the temperature

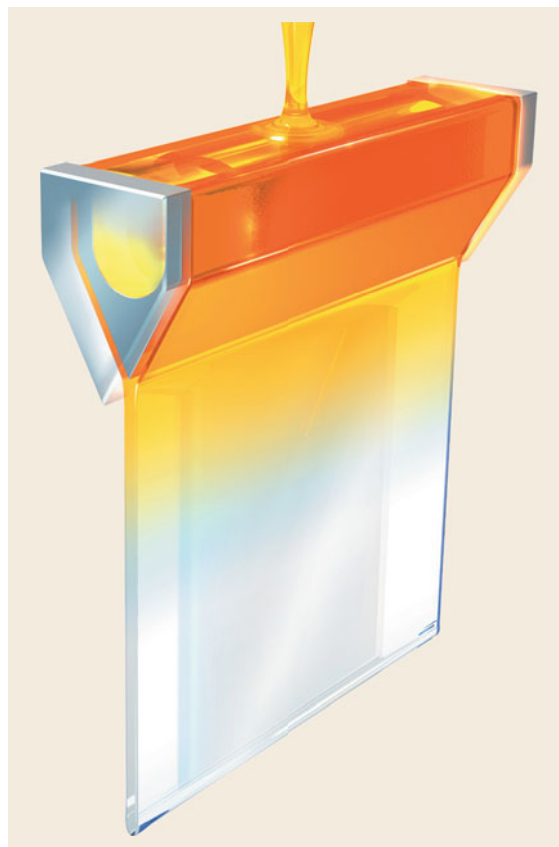


Fig. 45.14 Illustration of the fusion process. Courtesy Corning Incorporated

of the slot must be reduced to prevent runaway flow. Eventually, the temperature is too low, and the glass can devitrify, or the forming characteristics can exceed the operating window of the slot design. Even when refractory metals like Pt are used in the slot, the hydrostatic pressure head can slowly bow the slot open over time. In the fusion process, wear of the trough walls has little effect on flow or flow distribution, since it is an overflow design. The fusion process can also tolerate significant wear on the root as well without changing the sheet attributes. A video of the fusion process is available in [45.36].

While the fusion process provides the best surface quality of currently known forming processes, it is also the most demanding and limiting when it comes to glass composition. The glass needs to be pulled off the bottom of the isopipe faster than it falls to avoid U shaped ripples in the sheet called baggy warp. In other words, the pulling force on the sheet must exceed the gravitational force, which requires the glass to have a liquidus viscosity greater than 10^4 Pa.s. Only a small fraction of known glasses meet this challenging requirement, so

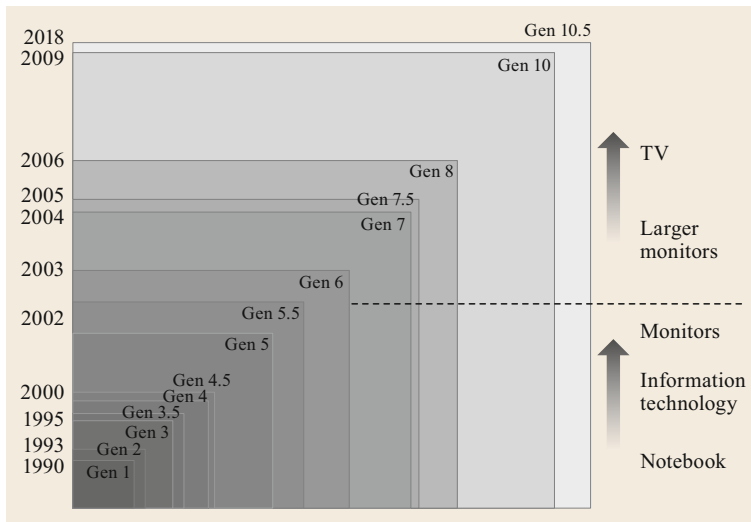


Fig. 45.15 Display substrate generation sizes over time. Courtesy Corning Incorporated

glass compositions have to be specially designed for fusion, as will be discussed in Sect. 45.5.

The fusion process has scaled well over time and advances in glass forming technology have kept pace with advances in the panel making industry. From the small $0.3\text{ m} \times 0.4\text{ m}$ Gen 1 display substrates in 1990, the process has gradually increased in size to the enormous $2.94\text{ m} \times 3.37\text{ m}$ Gen 10.5 sheets in 2018 shown in Fig. 45.15. Part of the reason why a-Si TFT-LCD won the display platform battle was because of its scalability and versatility, which were enabled by the ability of substrate makers to deliver larger and larger sheets (Table 45.1) without sacrificing attributes [45.37]. For the LCD watches, clocks, and gasoline pump indicators that made up the early market, $0.3\text{ m} \times 0.4\text{ m}$ Gen 1 substrates were adequate. However, the more devices a panel maker can fabricate on a sheet, the greater their economies of scale. The introduction of LCD notebooks and desktop monitors drove the Gen 1 size up to Gen 5. The LCD TV era began in 2003, and eight 32" or six 37" panels efficiently utilized the area of Gen 6 sheets, but 46 and 52" class TVs required Gen 7 and 8 sized substrates for low cost production. Today's Gen 10 sheets can host 24 32" panels, 15 42" panels, or 6 65" panels [45.11], as shown in Fig. 45.16. These sheets are so large, in fact, that they will not fit under many highway overpasses when loaded on a truck, so some glass factories are located adjacent to the panel maker to avoid shipping difficulties.

Ironically, fusion was two decades ahead of its time for display and languished for decades since the in-

Table 45.1 LCD substrate generation (Gen) size over time

Generation	Size ($l \times w$, cm)	Date introduced
1	30×40	1990
2	37×47	1993
3	55×65	1995
3.5	60×72	1995
4	68×88	2000
4.5	73×92	2000
5	110×130	2002
5.5	130×150	2002
6	150×180	2003
7	187×220	2004
7.5	195×225	2005
8	220×250	2006
10	288×313	2009
10.5	294×337	2018

tended windshield application did not work out because the newly developed float process was less expensive [45.38]. However, the fusion process was used to make photosensitive glass for sunglasses in the 1970s and then began making the first LCD glasses in the 1980s. Today, the fusion process supplies most of the world's LCD and OLED display glasses [45.34] as well as the chemically strengthened cover glasses that protect the display and enable rugged mobile touch screen devices [45.19]. After 50 years, the fusion process is now making glass for thinner, stronger, and lighter weight windshields for its originally intended automotive market [45.39]!

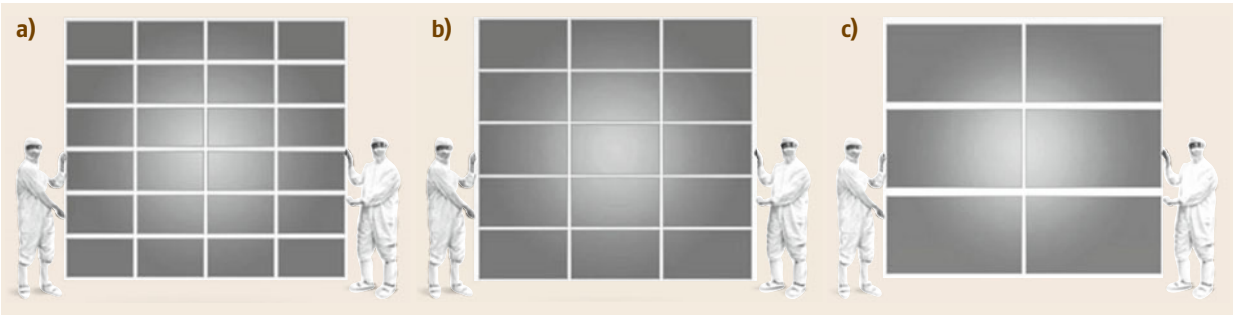


Fig. 45.16a–c Simulated layout of popular 16 : 9 LCD TVs on Gen 10 size substrates showing efficient area utilization and high throughput. Panel sizes are the nominal diagonal screen dimensions: **(a)** 24 32" panels, **(b)** 15 42" panels, and **(c)** 6 65" panels. Courtesy Corning incorporated

45.5 Glass Composition

The earliest TFT-based displays were small monochrome LCDs for watches, digital clocks, and calculators built on Corning 0211 alkali zinc borosilicate, because it was widely available in thin sheets and had lower alkali content than soda-lime-based silicate glass. Table 45.2 lists the properties of several glasses used for LCD and OLED displays. Even though the alkali content of 0211 was not high, it was still enough to impact the lifetime of the display, and the first alkali-free glasses were introduced in the 1980s. These alkaline earth borosilicates were based upon the anorthite, silica, pseudowollastonite eutectic marked as point B in Fig. 45.17. Nearly every LCD display glass made ever since is close to the anorthite-silica (cristobalite, tridymite, or quartz) cotectic between A and B with some B₂O₃ and a mix of alkaline earth oxides (MgO, CaO, SrO, BaO, and sometimes ZnO). Why is this composition region so fertile for LCD glass substrates? These glasses have the right combination of properties for Si-based electronics and are relatively easy to melt and manufacture. First,

they are free of alkalis that can migrate and poison thin film Si transistors. They have coefficients of thermal expansion that are very close to Si, which minimize thermal stresses on the electronics and prevent delamination or spalling. They also have 150–200 °C higher strain and annealing points than conventional soda-lime glasses, so the glasses can withstand higher processing temperatures, which enables better quality Si with higher mobility and better device performance, as listed in Table 45.2. Finally, the anorthite-silica cotectic between A and B has the lowest liquidus temperature in the ternary, and because these compositions are high in SiO₂, they are more viscous, so their liquidus viscosity is high enough to enable forming into precision sheet. Long before the first color liquid crystal displays were ever made, *Dumbaugh* and *Alpha* [45.40] realized that alkaline earth aluminosilicates were well suited for thin film Si-based transistors and engineered compositions designed for the task. So what are the key compositional drivers for LCD glasses and how can we tailor their properties? While most commercial

Table 45.2 Glass properties and year introduced

Glass	Strain point (°C)	Annealing point (°C)	Softening point (°C)	CTE (ppm/°C)	ρ (g/cm ³)	Young's modulus (GPa)	LCD market year
Soda-lime	500	550	730	8.7	2.5	70	–
Corning 0211	510	550	720	7.4	2.53	74	1967
Corning 7059	590	640	845	4.6	2.76	68	1984
Corning 1737	665	730	975	3.8	2.54	71	1993
EAGLE 2000®	665	720	985	3.2	2.38	71	2000
EAGLE XG®	670	720	970	3.2	2.38	74	2006
Jade®	735	785	1030	3.8	2.63	82.1	2008
LotusNXT®	750	805	1045	3.5	2.59	83	2015
Rare earth-containing	780	830	1045	3.8	2.84	88	–

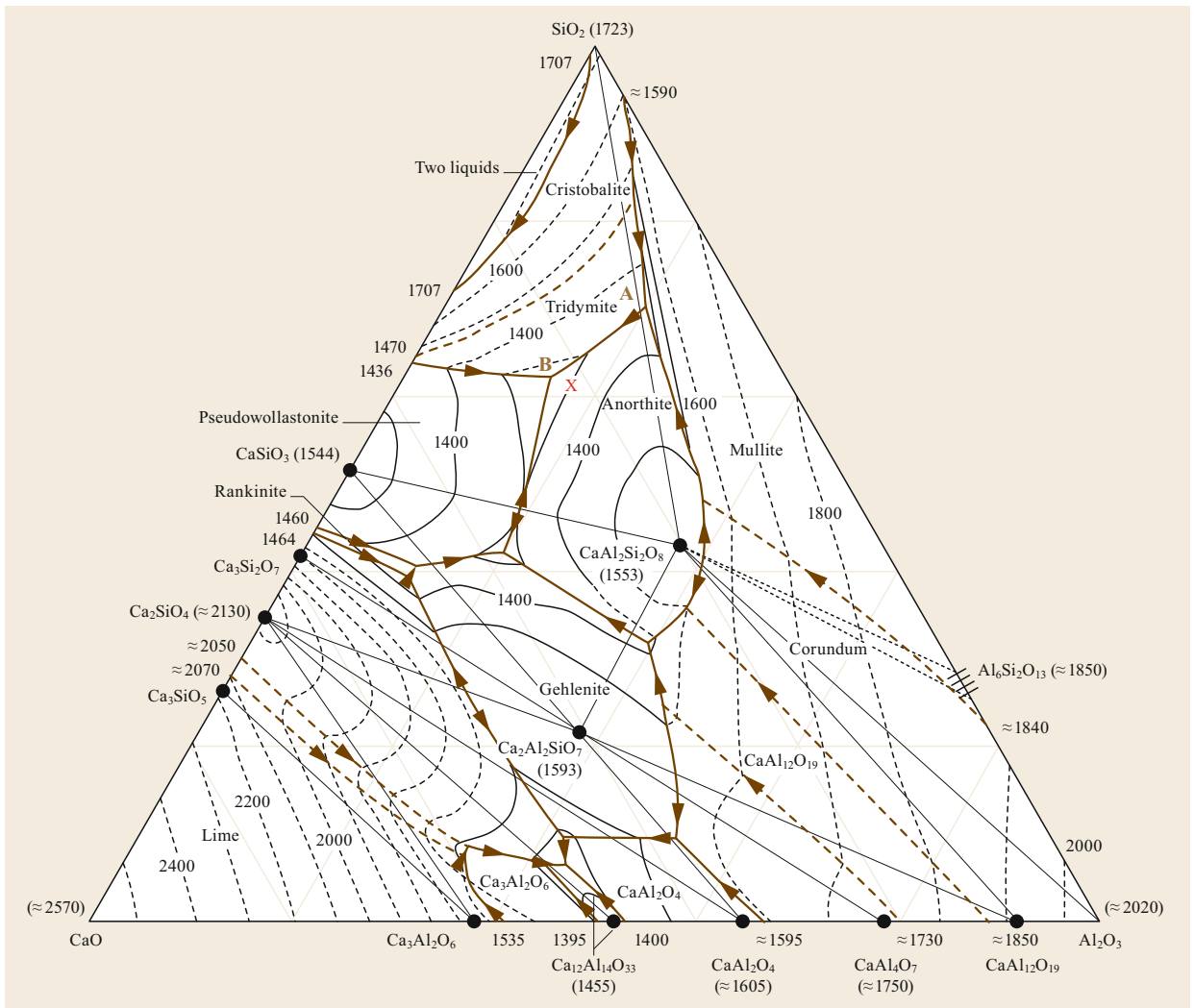


Fig. 45.17 CaO-Al₂O₃-SiO₂ phase diagram. All values are given in °C. After [45.41]

glasses contain eight or more intentional oxides, it is much easier to understand and visualize the complex property dependencies on composition by simplifying the composition to ternary diagrams, so they will be used extensively in the next section.

45.5.1 Liquidus

The liquidus is defined as the highest temperature where crystals will exist in equilibrium with the surrounding liquid [45.42]. Above this temperature, only the liquid phase exists, and the glass will never crystallize above the liquidus temperature. It is the most difficult property to optimize and predict because the liquidus surface is complex (Fig. 45.17) and has mathematical discontinuities at eutectics and cotectics, which are actually

the points of greatest interest, as will soon become apparent. It is also one of the most important properties for manufacturing because it dictates which forming process and temperatures can be used to make products [45.26]. Hence, liquidus is first on our list of properties to explore. The greater the viscosity of the glass, the more forming processes are available for forming. To be able to make flat pristine precision sheets via fusion, recall that the viscosity must exceed 10^4 Pa s. As shown in Fig. 45.10, the viscosity of any glass can be increased by lowering the temperature. However, once the liquidus temperature is reached, the glass can begin to devitrify, and crystals will grow especially on any static surface contacting the glass below the liquidus temperature. Thus, to avoid crystalline defects or inclusions in the pristine sheet, the glass must exit the forming system

and support its own weight (or float on a denser liquid) when it is still above its liquidus temperature. While the viscosity of the glass can be increased by increasing the SiO_2 content, it also becomes very difficult to melt and refine the glass, as discussed in Sect. 45.3. Thus, the best way to increase the liquidus viscosity of the glass is to decrease its liquidus temperature. To decrease the liquidus temperature, the thermodynamic activity of the devitrification components must be decreased. In other words, the offending components need to be diluted or shifted away from the composition of the devitrification crystals that form. For example, consider the composition X in Fig. 45.17 with an anorthite liquidus temperature of 1300°C . SiO_2 can be added to X to decrease the activity of anorthite, but we quickly cross into the tridymite (SiO_2) phase field, and further SiO_2 additions now increase the liquidus temperature. So, it can be far more effective to suppress anorthite by diluting the CaO with other alkaline earths like MgO , SrO , BaO , and sometimes ZnO . As CaO is replaced by BaO (keeping Al_2O_3 and SiO_2 the same), anorthite will be suppressed, and the liquidus temperature will decrease, so the liquidus viscosity will increase. Eventually, we can add too much BaO and run into celsian ($\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), so we resort to MgO , and SrO in a similar manner, coming up with the ideal mix of alkaline earth oxides. The red X will move straight down into the ternary until we hit the extension of the tridymite phase field. Now, we must either decrease the SiO_2 content or add something else to further suppress the liquidus. B_2O_3 is the perfect addition, since it is not compatible with any of the alkaline earth silicate crystal structures nor any of the SiO_2 polymorphs, so it effectively dilutes all of the troublesome phases and effectively lowers the liquidus temperature. With the appropriate mix of alkaline earths and B_2O_3 the liquidus temperature can be suppressed by roughly 200°C and the liquidus viscosity increased by orders of magnitude to enable fusion. Unfortunately, we cannot simply add as much B_2O_3 , as we want to suppress the liquidus because we have to balance other properties for the display maker as well as the ability to manufacture precision sheets. This is true for all glass constituents, and their impact on other properties will be explored next.

45.5.2 Annealing Point

Most glass properties are not as complex as liquidus and tend to vary in a much more systematic and predictable manner. Figure 45.18 shows the effect of composition on the annealing point ($10^{12.2}\text{ Pa s}$) of glasses in the $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ ternary system. The biggest driver is the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio with the SiO_2 content being a minor factor to increase the annealing point. As the

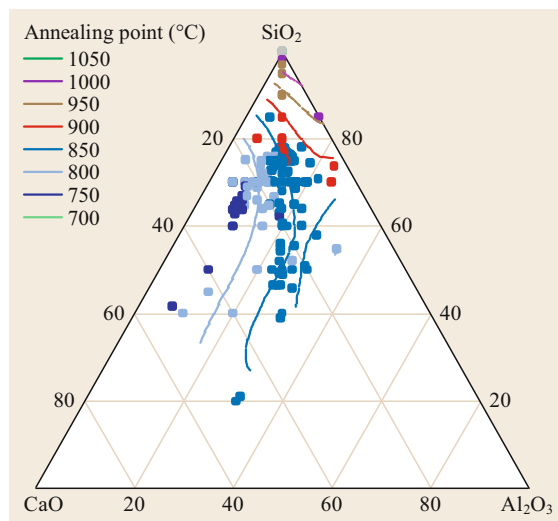


Fig. 45.18 Annealing point ($10^{12.2}\text{ Pa s}$) of glasses in the $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ ternary system

$\text{CaO}/\text{Al}_2\text{O}_3$ ratio increases, the annealing point of the glass decreases and vice versa. This is because alkaline earth oxides (RO) like CaO break up the glass network and create non-bridging oxygens, which lower the viscosity of the glass. Al_2O_3 counters this effect by consuming these non-bridging oxygens to make two AlO_4 tetrahedral units, each with four bridging oxygens, charge balanced by the Ca^{2+} ion to restore the network [45.43]. The identity of the alkaline earth does not matter immensely, and similar behavior is exhibited for all the alkaline earths. However, the smaller and higher the field strength of the alkaline earth ion, the higher the annealing point following the order $\text{MgO} > \text{CaO} > \text{SrO} > \text{BaO}$, so a MgO glass will have a higher annealing point than the analogous CaO glass. A mix of alkaline earths will also have a slightly lower annealing point than a simple mixing line would predict. However, almost all modern glasses will have a mix of alkaline earth ions because of its beneficial effect on the liquidus temperature, as discussed in the previous section. Liquidus will trump most other properties, since it does not matter how great a glass's properties may be if the glass is not manufacturable. Recall that liquidus is also one of the reasons why B_2O_3 is added to the glass even though it has a deleterious effect on the annealing point as shown in Fig. 45.19. So, even though annealing points of 900°C are attainable in the $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ system, by the time the composition is shifted to a reasonable liquidus temperature with less Al_2O_3 , a mix of alkaline earths, and the addition of B_2O_3 , the practical annealing points of most display glasses from 1980 until 2007 were around 720°C , as listed in Table 45.2. However, with the drive for higher performance, low tempera-

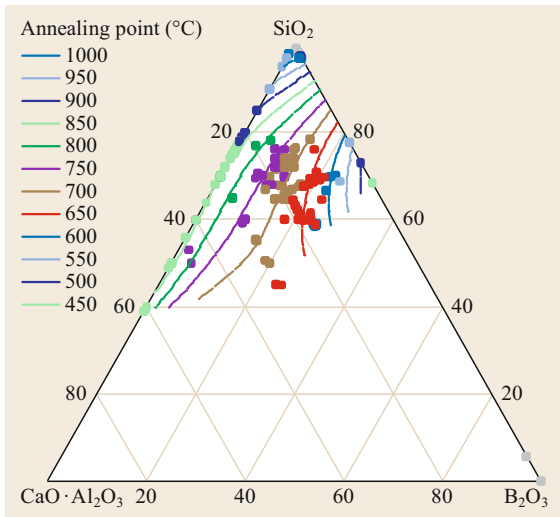


Fig. 45.19 Effect of B_2O_3 on the annealing point of the $CaO-Al_2O_3-SiO_2$ system

ture polycrystalline Si (LTPS) devices (such as high resolution LCDs and OLED devices for mobile and wearable technology) motivated glass researchers to deliver glasses with higher annealing points. These were around 790 °C in 2008 and have now broken the 800 °C barrier with today's high performance display glasses like Lotus NXT® [45.44], as shown in Table 45.2. The strain point ($10^{13.7}$ Pa s) is so close in viscosity to the annealing point that the compositional dependencies of the strain point are nearly identical and follow the same trends as the annealing point, just roughly 55 °C apart.

45.5.3 Softening Point

The softening point at $10^{6.6}$ Pa s is 5.5 orders of magnitude away from the annealing point and it is driven most strongly by the alkaline earth content, as shown in Fig. 45.20. The decrease in the softening point with CaO content is non-linear and is steepest at lowest alkaline earth content, and the decrease lessens at higher levels of CaO. Substituting other alkaline earth oxides for CaO has a similar effect to the annealing point with MgO lowering the softening point the least and BaO the most. Adding or increasing B_2O_3 will lower the softening point, just like it does for the annealing and strain points.

45.5.4 Thermal Expansion

The coefficient of thermal expansion (CTE) of the glass must be closely matched to that of the thin film Si transistors that will be deposited on the glass. The thermal

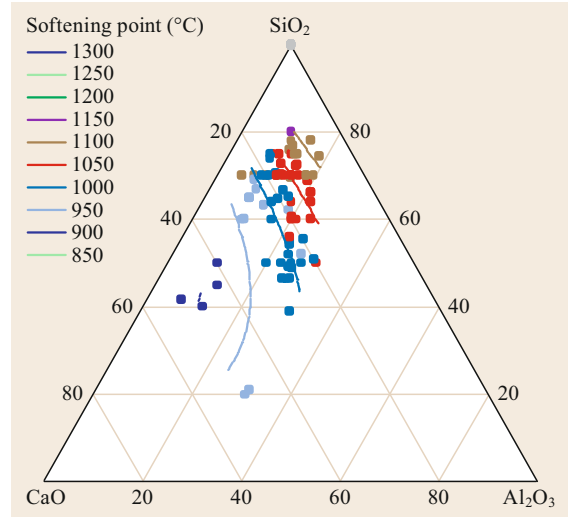


Fig. 45.20 Softening point of glasses in the $CaO-Al_2O_3-SiO_2$ ternary system

expansion coefficient of Si changes nonlinearly with temperature, but has an average CTE of 3.37 ppm/°C between room temperature and 300 °C [45.45–47]. Thus it is desirable to have a glass with a CTE near 3.4 ppm/°C. Of course, the CTE of Si increases with temperature and varies with the n-type or p-type dopants used. Furthermore, the gate oxides grown on the Si will also impact the thermal stresses developed on cooling, so the full temperature cycle and dopants and details of the TFT fabrication process need to be known to truly minimize thermal stresses between the TFTs and the substrate. However, each display manufacturer uses a different process with different temperatures and materials, which is rarely shared with glass manufacturers, so estimates are often used. Fortunately, the CTE of alkaline earth aluminosilicate glasses also increase with temperature similar to Si, so if the CTE of the glass is within about 0.7 of 3.37 ppm/°C, the thermal stresses that develop on cooling from TFT fabrication are small and generally acceptable.

Figure 45.21 shows that the CTE of compositions near the anorthite-silica cotectic are between 4 and 5 ppm/°C, so are too high for Si-based TFTs. However, there is a second benefit to adding B_2O_3 to decrease the liquidus temperature and that is a marked decrease in the thermal expansion coefficient. For glasses in the optimal zone for liquidus with 60–70% SiO_2 , B_2O_3 additions of about 10% drop the CTE from 4.0–4.5 to the target 3.5 ppm/°C as the composition moves from left to right across the diagram in Fig. 45.22. Figure 45.21 also indicates that the alkaline earth content is the biggest driver to increase CTE, so the mix of alkaline earth oxides also has a significant impact on CTE with

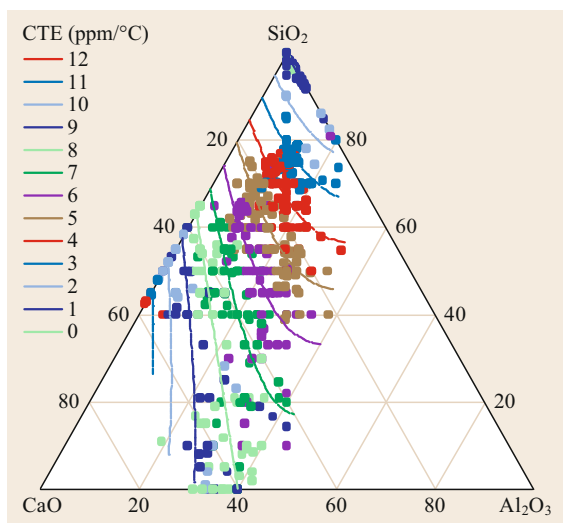


Fig. 45.21 Coefficient of thermal expansion of glasses in the CaO-Al₂O₃-SiO₂ ternary system

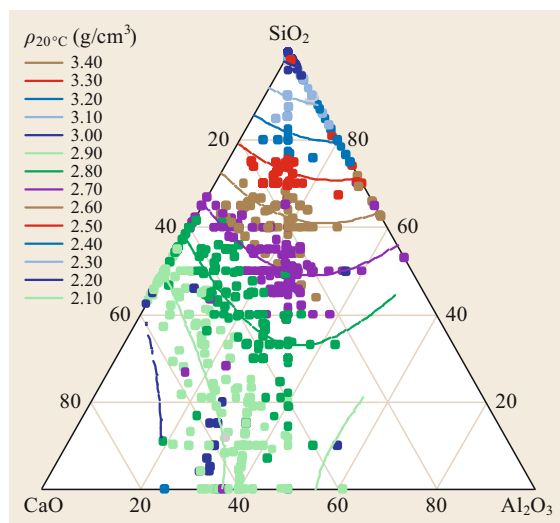


Fig. 45.23 Density of glasses in the CaO-Al₂O₃-SiO₂ ternary system

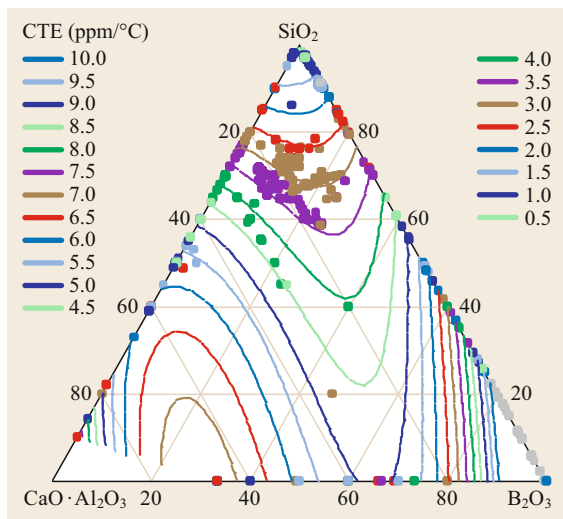


Fig. 45.22 Effect of B₂O₃ on the coefficient of thermal expansion of glasses in the CaO-Al₂O₃-SiO₂ system

MgO increasing CTE the least and BaO the most, following the usual series (MgO < CaO < SrO < BaO).

45.5.5 Density

Display makers prefer a glass with low density not only to decrease the weight of the final device, but also to decrease gravitational sag during processing, since the sheets are only supported on the edges during some processing steps. The density of alkaline earth aluminosilicates decreases with SiO₂ content, as shown in Fig. 45.23. The alkaline earth identity also has a strong impact on density and increases with the molecular

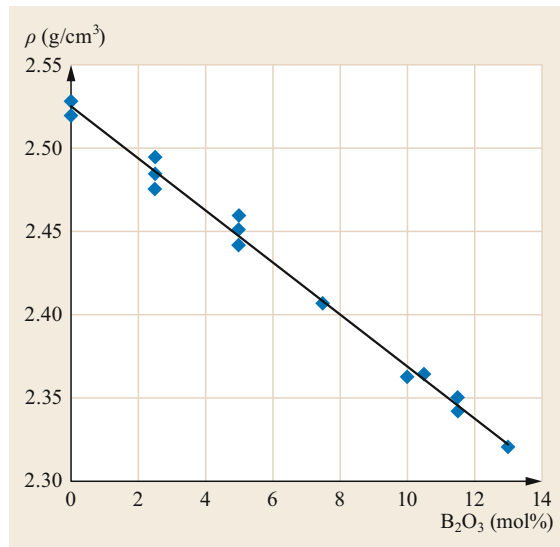


Fig. 45.24 Effect of B₂O₃ on the density of glasses in the CaO-Al₂O₃-SiO₂ system

weight of the alkaline earth oxide, so density will increase in the usual series (MgO < CaO < SrO < BaO). B₂O₃ is also a large lever for decreasing density, as illustrated in Fig. 45.24, but unfortunately it also decreases the modulus of the glass.

45.5.6 Young's Modulus

Display makers also prefer glasses with higher modulus because they are stiffer and will exhibit less elastic distortion and TPV, as explained in Sect. 45.2.2. Higher modulus glasses also sag less when only supported on

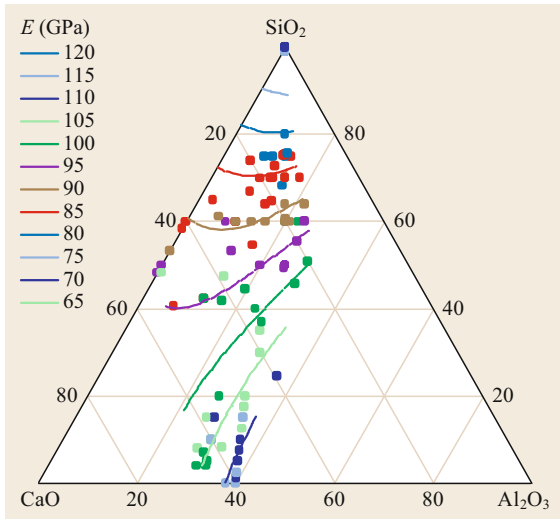


Fig. 45.25 Young's modulus E of glasses in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ternary system

the edges. The sag S of an elastic material is proportional to

$$S \propto \frac{L^4 \rho g (1 - \nu)^2}{t^2 E}, \quad (45.7)$$

where L is the unsupported span, ρ is the density, g is the gravitational constant, ν is Poisson's ratio, t is the thickness, and E is Young's modulus. As today's display substrates become thinner and thinner, the sag across a large sheet becomes appreciable. The variable distance from the processing equipment head to the substrate during device manufacture can either cause decreased precision or require more complex machinery to compensate for the sag. Higher modulus also decreases deflection of the device in use and better maintains the LC gap between the sheets. Figure 45.25 shows that the $\text{CaO} \cdot \text{Al}_2\text{O}_3$ content is the biggest driver to increase modulus and that increasing SiO_2 decreases the modulus. The mix of alkaline earths is also important and the modulus will increase in the usual series ($\text{MgO} > \text{CaO} > \text{SrO} > \text{BaO}$). Moreover, since the density increases in the opposite direction, gravitational sag will be doubly increased going from MgO to BaO due to the increase in density and decrease in modulus. B_2O_3 decreases the modulus, as shown in Fig. 45.26, but it also decreases density, so its effect on sag is not as dramatic as the heavy alkaline earth oxides.

45.5.7 Optical Properties

Display glasses should not distort the color or brightness of a display. Any stress in the glass sheet will give

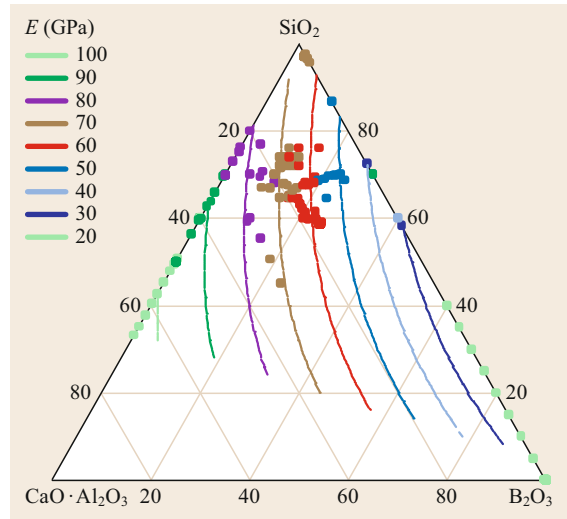


Fig. 45.26 Effect of B_2O_3 on Young's modulus E of glasses in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system

rise to birefringence. The stress multiplied by the stress optical coefficient of the glass equals the birefringence. Recall that LCDs work by polarization control, so any birefringence in the glass will rotate the polarization, lead to light leakage, and decrease the contrast ratio of the display. Thus, the birefringence of the glass sheet needs to be minimized. While the composition can be used to adjust the stress optical coefficient by about 10%, the stress can be reduced an order of magnitude by carefully cooling the glass uniformly to avoid differences in fictive temperature, shrinkage, and CTE. Thus, most manufacturers pay far more attention to glass processing than composition for controlling birefringence. Of course, birefringence is of little concern for unpolarized devices such as OLED displays.

Display glasses need to be transparent, so uniform high optical transmission $> 90\%$ from 400 to 700 nm is a must. Some processing and photolithography during device manufacturing is done in the UV at 365 nm, which requires at least 80% transmission down to 350 nm. The internal transmission of the glass in the visible portion of the spectrum is nearly unaffected by changes in the major oxide constituents (SiO_2 , Al_2O_3 , B_2O_3 , MgO , CaO , SrO , BaO) and will be dictated by the level of optically absorbing impurities, especially the ubiquitous transition metal contaminants including oxides of Fe and its neighbors V, Cr, Mn, Co, Ni, and Cu, so it is desirable to choose raw materials like sand, limestone, and aluminum oxide sources that contain less than 500 ppm of these impurities.

For light diffusing panels which guide light from the LEDs at the edges of the panel to the backplane of the LCD, these impurities must be kept below 100 ppm

to enable efficient transmission over the 1 m long path length to the center of today's large screen LCD TVs. Until 2016, polymer light-guide plates (LGP) were used to guide and distribute light from the LEDs at the edges evenly across the entire display. However, polymer LGPs swell with humidity and temperature, which can cause warping and compromise their opto-mechanical performance. Thus, designers had to incorporate a wide bezel, a thicker backlight, and air gaps to accommodate the swelling and shrinking of the polymer LGP. While glass is far more dimensionally stable and does not swell with humidity, the transmission and color shift of existing display glasses was not sufficient to evenly illuminate large TVs. However, Corning scientists designed a glass with low attenuation and high color purity that matches the best available polymers. This glass takes *slim* TVs from 15 mm thick with polymer LGPs and large bezels and enables narrow bezel 65" TVs that are less than 5 mm thick! This innovation received the 2016 Display Component of the Year award [45.48].

45.5.8 Durability

Display glasses need to stand up to impacts, drops, and thermal cycling, so they need to be mechanically strong. Since strength is dictated by surface flaws [45.19, 49], a pristine surface and well finished edges free of nicks and cracks is imperative. The fusion process provides a pristine surface that is untouched during the glass manufacturing process and is thus ideally suited. For mobile devices like smart phones and tablets, which are dropped and swiped far more than stationary LCD monitors and TVs, extra protection is provided by covering the display with a chemically strengthened cover glass, but that is the subject of other book chapters [45.19] and Chap. 8.

Display glasses also need to be chemically durable, not only to the environment, but to the manufacturing process itself. The display fabrication process can have more than seven thin film patterning steps and as many etching steps consisting of treatments by complex corrosive mixtures of acids, bases, and fluorides that the glass host must endure while portions of the Si, conductive pathways, and gate dielectrics are etched away [45.50]. With the exception of some specific acid solutions, the acid durability of glass generally improves exponentially with SiO₂ content. In contrast, a high B₂O₃ content tends to lower acid durability. To complicate the issue, many panel makers etch the glass to less than half of its original thickness after device fabrication to thin the display panel for lightweight and super thin displays for mobile devices. Thus, it is often desirable for the glass to etch quickly in one acid for chemical thinning of the panel, while being durable

in the corrosive gasses, plasmas, and solutions used to etch the Si, gate dielectrics, conductive paths, etc. This is especially difficult to do, since many of the solutions and processes are proprietary to the display maker and thus unknown to the glass designer.

45.5.9 Other Properties

There are many other properties of interest to LCD makers, like dielectric constant, loss tangent, resistivity, refractive index, dispersion, heat capacity, thermal conductivity, and hardness. However, it is already challenging enough to balance all the tradeoffs with the primary properties of concern that these secondary properties are typically not optimized and simply are what they are, although there can be exceptions for exotic devices where secondary properties are of primary importance.

45.5.10 Rare Earth Oxides

The rare earth oxides (oxides of Sc, Y, and the lanthanides La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) are chemically all very similar and, hence, hard to separate. They are useful in display glasses because they steepen the viscosity curve of alkaline earth aluminosilicates [45.51], as illustrated in Fig. 45.10, and increase Young's modulus. Relative to LotusNXT®, the viscosity curve pivots about the softening point as more rare earth oxide is added, meaning that the annealing and strain points are increased, which improves compaction and TPV performance, while the melting and fining temperatures are reduced, which makes melting and refining of rare earth oxide-containing glass easier. The rare earth oxides significantly increase the anneal and strain points of the glass to increase thermal stability and reduce TPV and compaction during elevated process conditions, while the higher modulus helps reduce elastic distortion. Replacing RO with La₂O₃ in alkaline earth aluminosilicates will raise the strain and annealing point by about 10 °C per mol%, as shown in Fig. 45.27, but there is a 0.09 ppm/°C per mol% penalty for also increasing the CTE, so a careful balance is required.

The choice of rare earth is important, since most rare earths including the oxides of Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, and Tm have absorption bands in the visible portion of the spectrum and can reduce the optical transmission of an LCD or fluoresce to create undesired light in the display or during photolithography. However, absorption is not a concern for the backplane glass for top emitting OLED devices. This leaves Sc, Y, La, Gd, Yb, and Lu as the most broadly

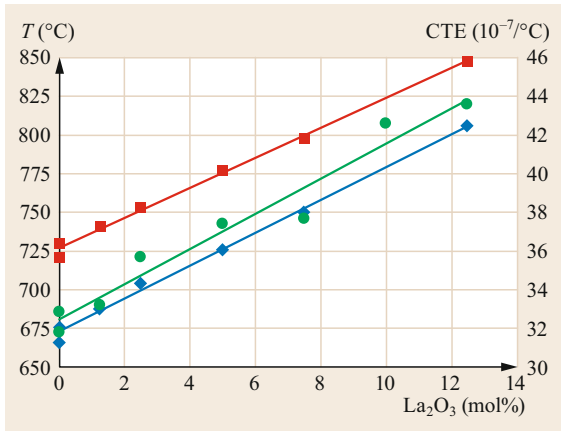


Fig. 45.27 Effect of La_2O_3 on strain point (diamonds), annealing point (squares), and CTE (circles)

useful rare earth oxides, with La and Y being the rare earths of choice, since they are the most abundant and least expensive options of the relatively costly rare earth family. Regardless of cost or color, the impact of the rare earth ion on glass properties scales with their ionic radius. Of the lanthanides, the ionic radius decreases as the atomic number increases [45.52, 53], with La^{3+} being the largest and Lu^{3+} the smallest, so Lu^{3+} will increase the modulus and steepen the viscosity curve the most, while La^{3+} will increase the modulus and steepen the viscosity curve the least.

The rare earths increase the CTE of alkaline earth aluminosilicates, and the trend in CTE is just the opposite of the modulus with the smaller rare earths increasing CTE the least and the largest ions increasing it the most. Density will simply scale with the atomic weight, so Lu_2O_3 will increase density the most and La_2O_3 the least. Sc is the smallest and lightest of the rare earths and provides the highest modulus, strain point, annealing point, and lowest CTE and density because of its small size, high field strength, and low molecular weight. However, it is prohibitively expensive, so Y is a more practical alternative with only a slight penalty in properties. While the addition of rare earth oxides lowers the viscosity above the softening point and lowers the viscosity in the liquidus regime, they fortuitously compensate by lowering the liquidus temperature. The alkaline earth aluminosilicates all have a high melting point (refractory) $\text{RO-Al}_2\text{O}_3\text{-}2\text{SiO}_2$ phase, as exemplified previously by anorthite in Fig. 45.17, while there are no ternary $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ phases in the analogous RE_2O_3 ternary [45.55] illustrated in Fig. 45.28. So, the liquidus is actually at a minimum near the middle portion of the $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ diagram unlike the $\text{RO-Al}_2\text{O}_3\text{-SiO}_2$ diagram.

Because rare earths lower the liquidus temperature, little or no B_2O_3 is needed in these compositions, so the B_2O_3 penalty for strain and the annealing point is avoided, and both are boosted by 30°C to 780 and 830°C, respectively, as listed in Table 45.2, yet the

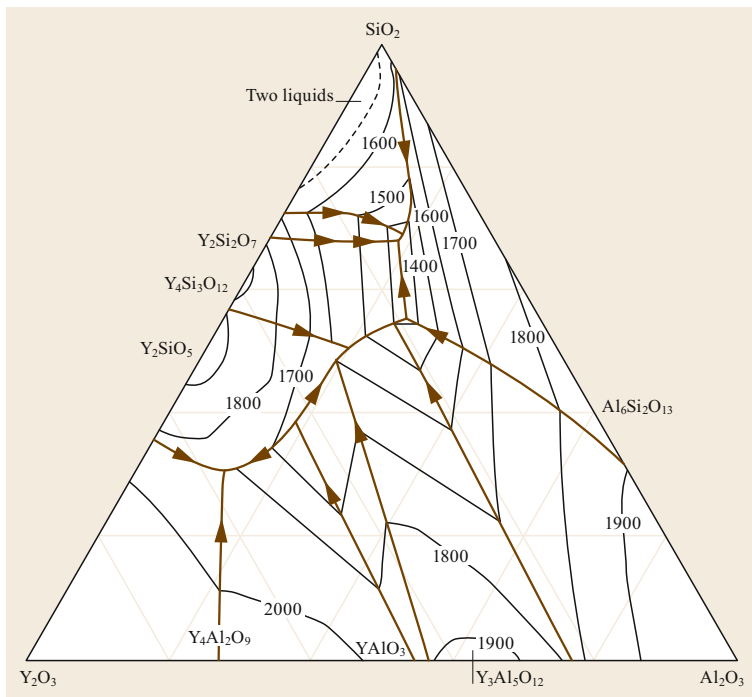


Fig. 45.28 $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ phase diagram. All values are given in °C. After [45.54]

glass is easier to melt. Rare earth oxides enable fusion formable glasses with strain points above 750 °C with only 2 mol% rare earth oxide addition, and higher rare earth oxide additions provide an even bigger benefit to melting temperature reduction, as shown in Fig. 45.29. This reduction in the melting and forming temperature can translate into longer tank and forming line life, which reduces time and cost. The rare earth-containing glasses also have a 5% benefit in modulus increasing stiffness and decreasing sag. However, there is a penalty in density and CTE for adding the heavier and larger rare earths, as listed in Table 45.2. Figure 45.30 shows that Y_2O_3 increases the modulus by approximately 1.8 GPa/mol%. The spread in the data about the trend line is caused by the impact of the various mixes of alkaline earths used in those compositions, since MgO has a more positive impact on modulus than BaO . La_2O_3 provides a modulus increase of roughly 1.4 GPa/mol%. This boost in modulus decreases thermal sag and elastic distortion.

45.5.11 Compositional Summary

Glass composition is a complex and delicate balance between multiple customer and manufacturing properties and attributes. While the increase or decrease of one oxide improves one property, it usually degrades three others, so all seven major constituents must be simultaneously optimized to obtain the best possible mix of attributes in a manufacturable composition. SiO_2 is by far the largest fraction of the glass, since it provides low density, low CTE, good durability, and high viscosity, and its concentration is typically in the vicinity of the alkaline earth aluminosilicate-silica cotectic. This

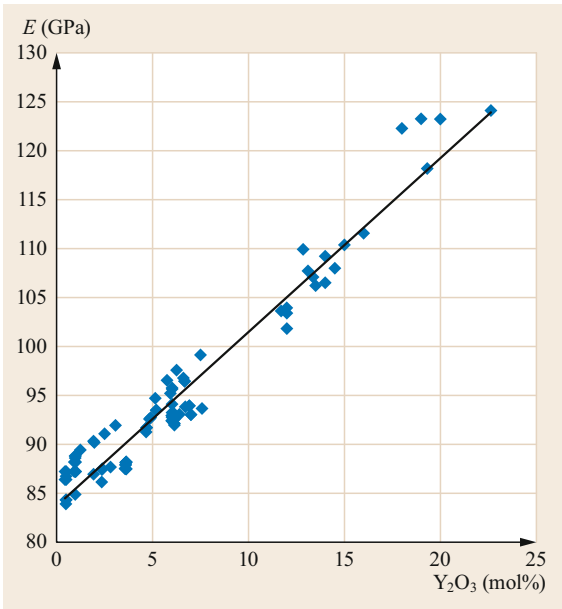


Fig. 45.30 Effect of Y_2O_3 content on Young's modulus

maximizes the liquidus viscosity, which enables fusion forming and gives rise to some of the most important product attributes:

- 1. A flat pristine surface
- 2. Uniform thickness
- 3. Low cost.

The alkaline earths help make the glass meltable, eliminating knots, stones, and melting defects, while their mix controls the liquidus, viscosity, annealing

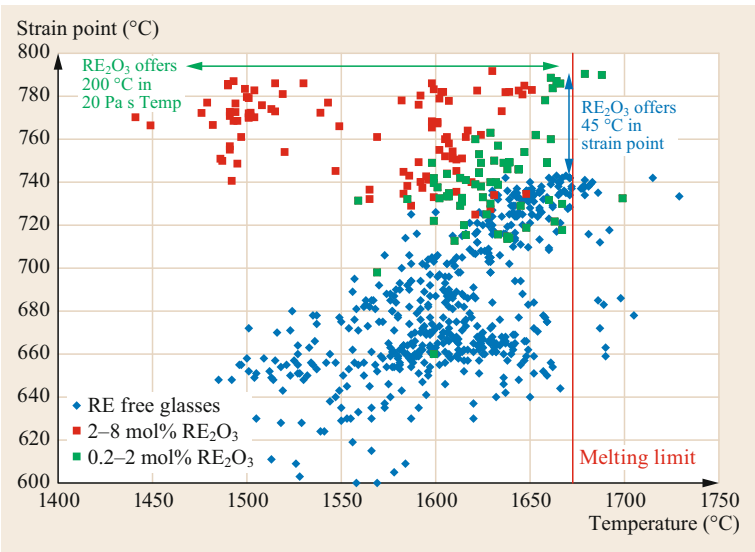


Fig. 45.29 Rare earth oxide additions enable higher strain points with lower temperature where viscosity is 20 Pa s

point, CTE, modulus, and density. The Al_2O_3 helps compensate for the low annealing point of alkaline earth rich glasses by consuming non-bridging oxygens and bolstering the glass network, which raises the modulus, annealing point, and viscosity, while lowering the CTE. B_2O_3 helps to lower the liquidus, density, firing temper-

ature, and CTE, but it also degrades the annealing point, durability, and Young's modulus of the glass. The rare earth oxides steepen the viscosity curve and boost the modulus, enabling very high strain point glasses that are easy to melt but that are expensive and increase the density and CTE of the glass.

45.6 Three-Dimensional (3-D) Upconversion Displays

Rare earth-doped glasses and glass-ceramics also make three-dimensional (3-D) upconversion displays possible [45.56–58]. In a 3-D upconversion display, two infrared laser beams of different wavelengths are intersected to create visible upconversion luminescence at the point of intersection. For the case of Pr^{3+} -doped glass, the first laser beam, at 1014 nm, excites every active ion in its path to the first excited state, $\text{Pr}^{3+} {}^1\text{G}_4$, as shown in Fig. 45.31. The 1014 nm laser can only excite to the first level and no further because there is no Pr^{3+} energy level 9862 cm^{-1} (energy of 1014 nm photon) above the metastable ${}^1\text{G}_4$. Then, the second laser beam at 850 nm will only excite Pr^{3+} ions already in the ${}^1\text{G}_4$ to the ${}^3\text{P}_2$ level (excited state absorption), which will quickly non-radiatively decay to the ${}^3\text{P}_0$ and then emit blue light as the excited ion returns to the ground state. Similar schemes can be used with Tm^{3+} and Er^{3+} -doped glasses to create blue and green emissions.

At higher Pr^{3+} concentrations, one excited ion in the ${}^3\text{P}_0$ state will cross relax with a nearby ion in the ${}^3\text{H}_4$ ground state, dropping the first ion to ${}^1\text{D}_2$ and exciting the second ion to ${}^3\text{H}_6$. The ion in the ${}^1\text{D}_2$ state

will then radiate red light, as shown in Fig. 45.31. There is no 850 nm absorption (no level near $11\,760\text{ cm}^{-1}$) in unexcited Pr^{3+} , thus upconversion will only take place where the two beams intersect. This process of sequentially absorbing two photons of different wavelengths (or energies) by the same ion is called two-frequency upconversion. In this manner, any location in 3-D space within the rare earth-doped glass or glass-ceramic can be addressed by scanning the 850 and 1014 nm laser beams to intersect at that location and cause visible fluorescence [45.57]. To create full color RGB displays, Pr^{3+} can be used for red, Er^{3+} for green, and Tm^{3+} for blue [45.56] emission, although there are other possibilities. The fluorescence lifetime of these rare earths in the visible portion of the spectra is on the order of milliseconds, so if the lasers are scanned on the order of 1000 Hz, the image is continuous and flicker free. Laser arrays are also possible to simultaneously address multiple pixels without the need for steering optics. Unlike stereoscopic 3-D displays, which send different images to the left and right eye creating virtual images, 3-D upconversion displays create real 3-D

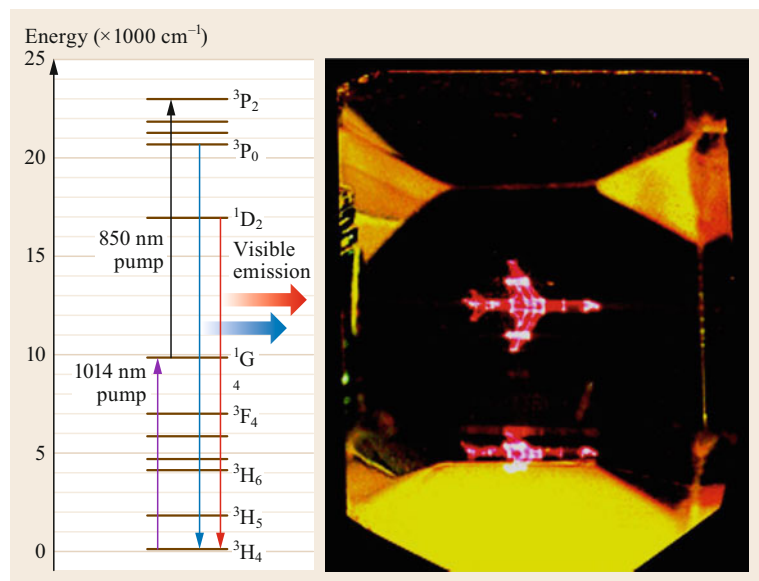


Fig. 45.31 Pr^{3+} upconversion scheme for 3-D display and resulting 3-D image. Reproduced with permission [45.56, 57]. Photo courtesy E. Downing

images that can simultaneously be viewed by multiple observers without the need for special glasses or headgear. These devices are not yet commercially viable due to complexity and expense, but are quite impressive in operation and may one day be useful for 3-D rendering of medical images, air traffic control, or entertainment.

Stereoscopic 3-D TVs typically use either passive polarization or active shutter to send left and right eye signals. For passive polarization led by LG and Vizio, left and right eye images are displayed with orthogo-

nal polarizations, and the viewer wears a pair of glasses with the left eye polarized in one direction and the right eye polarization rotated 90° to separate the two images. For active shutter, the left and right eye images are displayed sequentially in time, so the viewer's glasses are actually shutters that turn on and off sequentially and are synched to the TV to display left and then right images in fast succession. Neither of these technologies change the requirements on the glass, and both are falling out of favor, so they will not be discussed further [45.59].

45.7 Electronics on Glass

The processing time required to crystallize amorphous Si into higher mobility and performance polycrystalline Si decreases exponentially with temperature above 800 °C, as illustrated in Fig. 45.32. These temperatures would soften most early display glasses in Table 45.2, cause unacceptable compaction, TPV, and permanently deform them due to thermal sag. However, new rare earth-containing glasses can easily survive temperatures up to 850 °C, where the Si can now be annealed in reasonable time to increase mobility and device performance. Figure 45.33 shows the performance of Si transistors grown at 600 and 900 °C. Note that 5 V is plenty to switch the transistor current grown at 900 °C by 6 orders of magnitude from the off to the on state, while the transistor grown at 600 °C requires more than 10 V to change the current by 6 orders of magni-

tude. The transistor grown at 600 °C has lower electron mobility, inferior current voltage performance, and is unsuitable for high end devices.

Not only can the Si be crystallized at these temperatures, but as Fig. 45.32 shows, the crystals can be annealed and defects healed in a few tens of minutes at 830 °C. This will further increase the electron mobility and transistor performance. Finally, gate oxide layers can be grown in this temperature regime by oxidizing the Si. At 830 °C, 10 nm of SiO₂ can be thermally grown in about an hour. While these polysilicon devices do not have as high mobility and performance as single crystal Si devices and are not quite suitable for CPUs, they are sufficient for drivers, interfaces, and memory, so that these devices can be

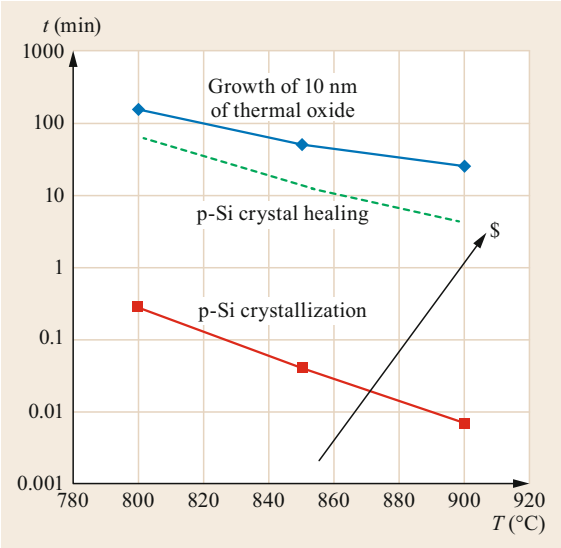


Fig. 45.32 Time required to crystallize, anneal, and grow thermal oxide on p-Si as a function of temperature

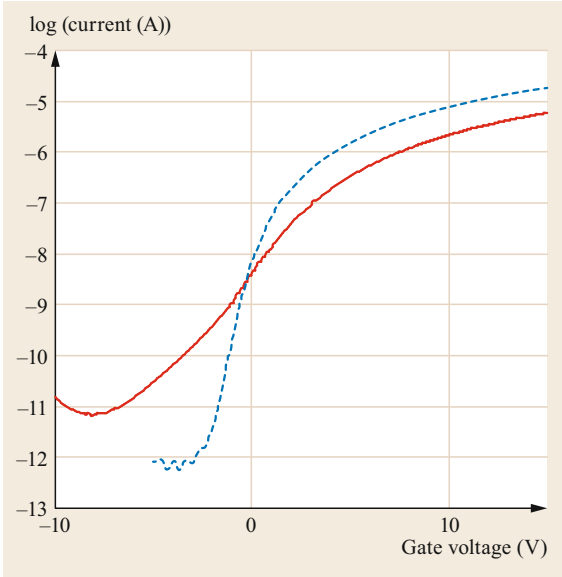


Fig. 45.33 Performance of Si transistors grown at 600 °C (solid curve) and 900 °C (dashed curve)

integrated directly onto the display glass simplifying design, increasing reliability, and reducing cost. It is also possible to make single crystal Si devices on these high strain point glasses by anodically bonding single crystal Si or Ge to the glass and then processing the electronics just as if it were on a wafer, so that the

entire computer could be integrated on the glass substrate [45.60, 61]. High strain point transparent glass-ceramics are also suitable for making single crystal devices on glass [45.61, 62]. The downside to transparent glass-ceramics and rare earth-containing glasses is their increased cost.

45.8 Flexible Glass and Displays

Most people do not think of glass as a flexible material even though they may have experienced glass wool, fiberglass insulation, and fiber optics because the bulk of their glass experience has been with thick brittle containers, windows, and cell phone covers. The resistance to bending or flexural rigidity (D) decreases with the thickness (t) cubed according to

$$D = \frac{Et^3}{12(1-\nu)^2}, \quad (45.8)$$

where E is Young's modulus, and ν is Poisson's ratio. Thus, the flexibility quickly increases as the glass becomes thinner, and quite bendable glass is possible, as shown in Fig. 45.34. Most polymers have approximately 20 times lower modulus than glass, and hence, are much more flexible [45.63]. However, polymers are much more prone to scratching, cannot tolerate high temperatures for deposition of Si-based electronics, and are not hermetic, so they cannot protect sensitive OLED-based devices from moisture. So, glass is still

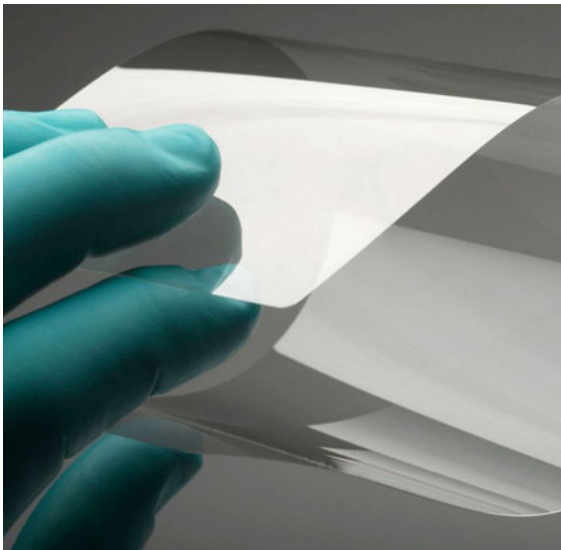


Fig. 45.34 Flexible Willow® glass. Courtesy Corning Incorporated

desired for flexible displays. Flexible glass is nothing new. *Corning* developed a composition and process to make spools of glass only 25 μm thick in the early 1940s to make capacitors [45.64]. Today, the process has been scaled up from the 25 mm wide ribbons used to replace the natural mica for capacitors, to 1300 mm wide ribbons of flexible glass with up to 300 m length wound on a spool [45.65]. Nippon Electric Glass Co., Ltd. (NEG) has even made transparent flexible displays using two 30 μm thick sheets of its G-Leaf™ ultrathin glass to encapsulate the device [45.66]. Spools of flexible glass enable continuous roll-to-roll processing for high throughput, low cost manufacturing and may enable many devices such as photovoltaics, electronic circuit substrates, sensors, OLED lighting, and flexible displays from LCD to OLED to e-paper [45.64]. However, to be competitive, display fabs need to be large, and most of today's display making infrastructure is built around rigid display panels and batch processing, so investors want to recoup their investment before starting over with roll-to-roll processing.

Thus, many flexible display manufacturers actually use rigid display lines to manufacture their flexible displays instead of building new roll-to-roll lines to best utilize their existing assets. Even though the final flexible display may or may not have display glass in it, the manufacturing process still uses glass in both cases. Figure 45.35 compares the process flow for making rigid and flexible OLED displays. Samsung display builds their super AMOLED devices on Lotus™ NXT glass [45.67] and then lifts them off using laser debonding [45.68]. The rigid Lotus™ NXT substrate provides a very flat and smooth surface with excellent dimensional stability and uniform UV transparency for uniform laser lift off of the finished device from the substrate. Since these displays are of high resolution, they require tiny features, high performance transistors, and precision patterning, so the substrate needs to provide extreme dimensional stability and reproducibility over the entire temperature cycle of the OLED fabrication process and low TPV, as discussed in Sect. 45.2.2. The high modulus minimizes sag and distortion while the high annealing point minimizes TPV.

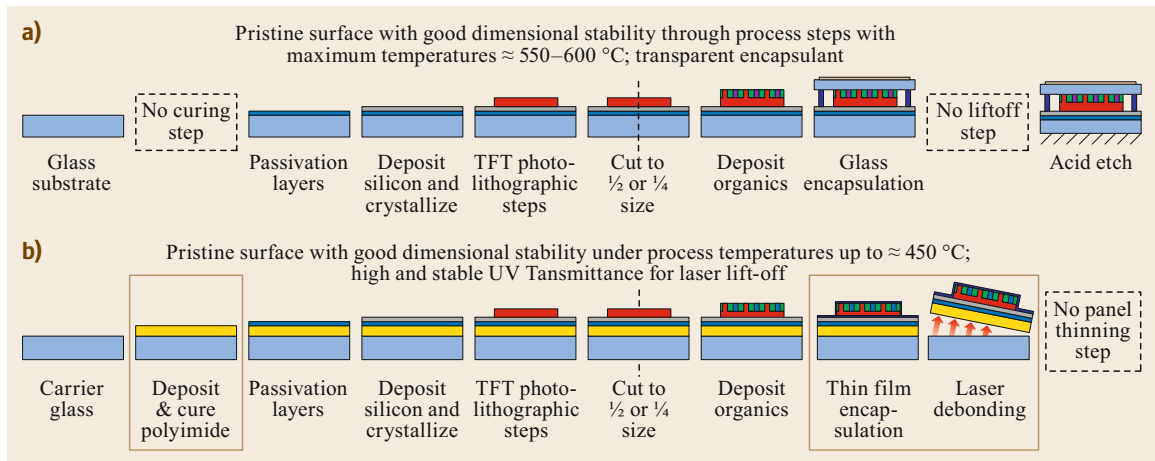


Fig. 45.35a,b Comparison of (a) rigid and (b) flexible LTPS-OLED process

Sisk et al. [45.68] provides more details and a good comparison of the flexible and rigid OLED processes.

After thin film encapsulation and liftoff, the flexible display can then be curved or bent and bonded to the curved cover glass of mobile devices like the Samsung Galaxy S8 [45.67] or the iPhone X [45.69]. So, currently the manufacturer gets to do all the flexing of the flexible display, while the consumer can only dream of foldable smart phones [45.70], flexible wearables, and roll-up TV's. So why aren't flexible displays prevalent? The short answer is reliability. While the flexibility of a sheet increases inversely with the thickness cubed, the stress on the surface of a bent sheet of glass only falls off linearly with the thickness [45.71], so even though the glass is flexible, the glass cover is still under a large bending stress and there is too little thickness for ion exchange to provide a very significant compressive layer. Polymers are lower modulus, so they take the bending well, but the hermetic encapsulants can fail after repeated bends, sharp contact, or blunt force allowing moisture to penetrate and destroy the device. Thus, the devices are usually only bent once and then mounted into a rigid curved device (as shown in Fig. 45.36) where the delicate thin display is protected from scratching and mechanical abuse that can initiate small flaws that could then lead to failure on the

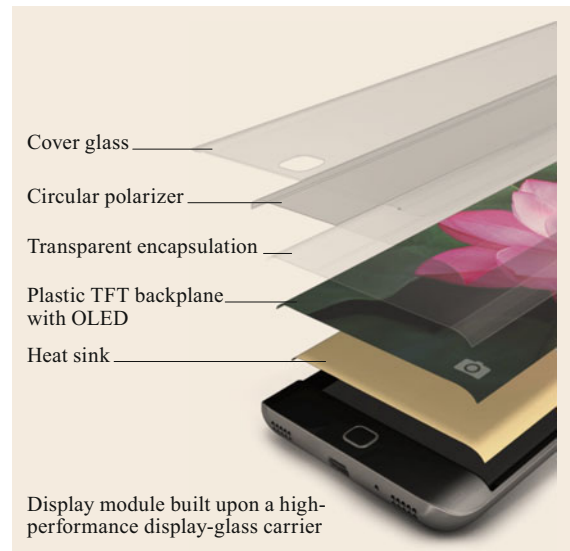


Fig. 45.36 Stack-up schematic of flexible OLED display used to make a curved device. Courtesy Corning Incorporated

very next flex. These issues need to be resolved before consumers can have flexible displays rolled up in a pen that last for more than a few uses.

45.9 Conclusions

Flat panel displays have infiltrated almost every aspect of our lives, with displays on our walls, in our vehicles, and in our pockets. Panel makers have continuously pushed beyond perceived limitations to make brighter, faster, bigger, higher contrast, and higher resolution dis-

plays than was thought possible just 25 years ago when CRTs still dominated the display market. The higher performance, lower cost, and lower power consumption of LCD displays increased their reach from simple monochrome alpha numeric readouts on watches and

gas pumps to full color brilliant displays on monitors, TVs, automobiles, cameras, cell phones, and all the way back to (smart) watches. Most of these advancements would not have been possible without the large innovations made in glass composition and forming. Larger and thinner sheets of higher temperature, alkali-free, stiffer glasses, with lower TPV and precision surfaces enabled displays to enrich many aspects of our daily life. Flat panel display demand is poised to hit 210 million m² in 2018 [45.72], or enough to cover 30 000 soccer fields. Since most display devices use at least two pieces of glass, and yields are always less than 100%, the demand for display glass will be more than double that amount. The next generation of displays will surely have better performance, integrate more functions, and reach even more applications, such as appliances, gadgets, large signage, automotive, architecture, home décor, displays integrated with fabrics, and augmented or virtual reality displays. The viral videos *A Day Made of Glass* [45.73] and *A Day Made of Glass 2* [45.74] show what the future of display glass may hold. Sizes will continue to grow, while curved and flexible displays will likely penetrate more of the market in the years ahead. OLED will continue to capture a market share at the expense

of LCD [45.75]. More of these devices will be touch enabled, thinner, and more connected in the future, offering greater functionality. While 8 K TVs are readily available, their content is scarce and technologically challenging to deliver. Their 33 megapixel images at 120 frames per second require 48 Gb/s bandwidth or 500 Mbps compressed, so advancements in multichannel broadcasting and content delivery are required. With 8 K, resolution is nearing the point where the human eye can no longer perceive future improvements, so performance enhancements in other areas like brightness, contrast, color gamut, 3-D, and speed are likely. The exception is near eye displays like those used in virtual and augmented reality devices, where increased resolution makes a perceptible difference. These new applications and enhancements will require continuous innovations in panel making (such as flexible and/or transparent displays and roll-to-roll processing), and a concomitant suite of new glass substrates will enable these inventions. While considerable innovation has already been delivered in the composition and manufacturing of glass substrates since the inception of the flat panel displays several decades ago, we expect this to remain a fruitful and exciting field for years to come.

References

- 45.1 M. Graham, A. Shuldiner: Corning and the military: Innovation in an era of permanent mobilization. In: *Corning and the Craft of Innovation* (Oxford University Press, Oxford 2001) pp. 173–278
- 45.2 L. Neikirk: Plasma TV is officially dead: The last plasma manufacturer has thrown in the towel, <http://televisions.reviewed.com/news/plasma-tv-is-officially-dead> (2014)
- 45.3 J.K. Willcox: Plasma TV is dead, so go buy one. Samsung pulls the plug on plasma, leaving LG as the sole plasma brand, <http://www.consumerreports.org/cro/news/2014/07/plasma-tv-is-dead-so-go-buy-one/index.htm> (2014)
- 45.4 J. Chen, W. Cranton, M. Fihn: *Handbook of Visual Display Technology* (Springer, Berlin 2012)
- 45.5 D. Hsieh: QLED: Quantum dot OLED or quantum dot LCD with LED backlight, or both?, <http://blog.ihs.com/qled> (2016)
- 45.6 G. Morrison: How QLED TV could help Samsung finally beat LG's OLEDs. Samsung is developing TVs based on quantum dot LEDs, pinpricks of light that promise even better picture quality than OLED TVs, <https://www.cnet.com/news/how-qled-tv-could-help-samsung-finally-beat-lgs-oleds/> (2016)
- 45.7 R. Triggs: Display technology explained: A-Si, LTPS, amorphous IGZO, and beyond, <http://www.androidauthority.com/amorphous-igzo-and-beyond-399778/> (2016)
- 45.8 L.K. Baxter: *Capacitive Sensors: Design and Applications* (Wiley-IEEE, Piscataway 1997)
- 45.9 R. Larsen: Touch technology in smartphones explained, <http://www.flatpanelshd.com/focus.php?subaction=showfull&id=1348049303> (2012)
- 45.10 R.J. Araujo, N.J. Binkowski: Alkali metal ion migration control, US Patent (Application) 5578103 (1996)
- 45.11 P. Bocko: Glass substrates for AMLCD, OLED and emerging display platforms. In: *Handbook of Visual Display Technology*, ed. by J. Chen, W. Cranton, M. Fihn (Springer, Berlin 2012) pp. 599–623
- 45.12 G.C.A.M. Janssen, M.M. Abdalla, F. van Keulen, B.R. Pujada, B. van Venrooy: Celebrating the 100th anniversary of the Stoney equation for film stress: Developments from polycrystalline steel strips to single crystal silicon wafers, *Thin Solid Films* **517**, 1858–1867 (2009)
- 45.13 S.M. Rekhson, O.V. Mazurin: Stress and structural relaxation in Na₂O–CaO–SiO₂ glass, *J. Am. Ceram. Soc.* **57**, 327–328 (1974)
- 45.14 S.-R. Ryu, M. Tomozawa: Structural relaxation time of bulk and fiber silica glass as a function of fictive temperature and holding temperature, *J. Am. Ceram. Soc.* **89**, 81–88 (2006)
- 45.15 A. Einstein: *Investigation on the Theory of the Brownian Movement* (Dover, New York 1926)
- 45.16 J. Brillo, A. Pommrich, A. Meyer: Relation between self-diffusion and viscosity in dense liquidus: New

- experimental results from electrostatic levitation, Phys. Rev. Lett. **107**, 1–4 (2011)
- 45.17 F.E. Wooley: Melting/fining. In: *Engineered Materials Handbook Ceramics and Glasses*, Vol. 4, ed. by S. Schneider (ASM International, Materials Park 1991) pp. 386–393
- 45.18 D.C. Boyd, D.A. Thompson: Glass. In: *Encyclopedia of Chemical Technology*, 3rd edn., Vol. 11, ed. by J.I. Kroschwitz, A. Seidel (Wiley, Chichester 1980) p. 807
- 45.19 M.S. Pambianchi, M. Dejneka, T. Gross, A. Ellison, S. Gomez, J. Price, Y. Fang, P. Tandon, D. Bookbinder, M.J. Li: Corning incorporated: Designing a new future with glass and optics. In: *Materials Research for Manufacturing*, ed. by L. Madsen, E. Svedberg (Springer, Cham 2016)
- 45.20 R. Doremus: *Glass Science* (Wiley, New York 1973)
- 45.21 A. Ellison, C. Cornejo: Glass substrates for liquid crystal displays, Int. J. Appl. Glass Sci. **1**(1), 87–103 (2010)
- 45.22 K. Kim: Redox reaction of multivalent ions in glass melts, J. Korean Ceram. Soc. **52**, 83–91 (2015)
- 45.23 E. Fourcault: Aparatus for the manufacture of plate glass by stretching, Patent US717378 (1902)
- 45.24 M. Cable: Mechanization of glass manufacture, J. Am. Ceram. Soc. **82**, 1093–1112 (1999)
- 45.25 I. Colburn: Method and apparatus for drawing sheet glass, Patent US860528 (1903)
- 45.26 H. Stevens: Forming. In: *Engineered Materials Handbook: Ceramics and Glasses*, Vol. 4, ed. by S. Schneider (ASM International, Materials Park 1991) pp. 394–401
- 45.27 D.N. Brown: Sheet glass forming apparatus, Patent US2422466A (1947)
- 45.28 R. Mauch, H. Wegener, A. Kruse, N. Hildebrand: Thin glass substrates for mobile applications, Proc. SPIE **4102**, 162–168 (2000)
- 45.29 H. Bessemer: Certain improvements in the manufacture of glass, Patent Br. 12101 (1848)
- 45.30 L.A.B. Pilkington, K. Bickerstaff: Manufacture of flat glass, Patent US2911759A (1959)
- 45.31 L.A.B. Pilkington: Review lecture: The float glass process, Proc. R. Soc. A **314**, 1 (1969)
- 45.32 T. Kloss, G. Lautenschlager, K. Schneider: Advances in the process of floating borosilicate glasses and some recent applications for specialty borosilicate float glasses, Glass Technol. **41**, 177–181 (2000)
- 45.33 Asahi Glass Co. Ltd: Asahi glass starts commercial production of new alkali-free glass for TFT-LCDs, <http://www.agc.com/en/news/detail/19980414.html> (1998)
- 45.34 Y.S. Choi, J.U. Yun, S.E. Park: Flat panel display glass: Current status and future, J. Non-Cryst. Solids **431**, 2–7 (2016)
- 45.35 S.M. Dockerty, G.C. Shay: Downflow sheet drawing method and apparatus, Patent US3149949A (1964)
- 45.36 Corning Incorporated: The fusion process: At the core of Corning's glass innovations, <http://www.corning.com/worldwide/en/products/display-glass/how-it-works.html> (2012)
- 45.37 P. Bocko: The challenges of higher-generation glass, Inf. Disp. **19**, 12–15 (2003)
- 45.38 M. Graham, A. Shuldiner: Reinstitutionalizing R&D: TV, Corning ware, and the search for breakthroughs. In: *Corning and the Craft of Innovation* (Oxford University Press, Oxford 2001) pp. 260–267
- 45.39 Corning Incorporated: Gorilla glass for automotive: Driving innovation, <http://www.corning.com/gorillaglass/worldwide/en/applications/automotive.html> (2016)
- 45.40 J.W. Alpha, W.H. Dumbaugh: Thin silicon film electronic device, Patent US4180618 (1975)
- 45.41 E.F. Osborn, A. Muan: *Fig. 630 CaO–Al₂O₃–SiO₂ in Phase Equilibria Diagrams*, CD-ROM Database, NIST Standard Reference Database, Version 4.1 (The American Ceramic Society, Westerville 2014), <https://www.nist.gov/srd/nist-standard-reference-database-31>
- 45.42 ASTM C829–81(2015): *Standard Practices for Measurement of Liquidus Temperature of Glass by the Gradient Furnace Method* (ASTM International, West Conshohocken 2015)
- 45.43 W.D. Kingery, H.K. Bowen, D.R. Uhlmann: *Introduction to Ceramics* (Wiley, New York 1976) pp. 91–100
- 45.44 Corning Incorporated: Corning Lotus™ NXT glass for high-performance displays, <http://www.corning.com/worldwide/en/products/display-glass/products/corning-lotus-nxt-glass.html> (2016)
- 45.45 R. Roberts: Thermal expansion reference data: Silicon 300–850 K, J. Phys. D **14**, L163–L166 (1981)
- 45.46 C. Swenson: Recommended values for the thermal expansivity of silicon from 0 to 1000 K, J. Phys. Chem. Ref. Data **12**, 179–182 (1983)
- 45.47 H. Watanabe, N. Yamada, O. Masahiro: Linear thermal expansion coefficient of silicon from 293 to 1000 K, Int. J. Thermophys. **25**, 221–236 (2004)
- 45.48 Corning Incorporated: Corning Iris™ glass: High-transmission light-guide plate enabling display thicknesses less than 5mm, <http://www.corning.com/worldwide/en/products/display-glass/products/corning-iris-glass.html> (2016)
- 45.49 J.S. Olcott: Chemical strengthening of glass, Science **140**, 1189–1193 (1963)
- 45.50 P. Bocko, C. Rosenblatt, L. Morse: Chemical durability and cleaning of flat panel display substrate glasses, SID Symp. Dig. Tech. Pap. **21**, 73 (1990)
- 45.51 B.G. Aitken, M.J. Dejneka, A.J. Ellison, T.E. Paulson: High strain point glasses, Patent US7612004 (2009)
- 45.52 Y.Q. Jia: Crystal radii and effective ionic radii of the rare earth ions, J. Solid State Chem. **95**, 184–187 (1991)
- 45.53 R.D. Shannon, C.T. Prewitt: Effective ionic radii in oxides and fluorides, Acta Crystallogr. B **25**, 925 (1969)
- 45.54 I.A. Bondar, F.Y. Galakhov: *Fig. 2586 Y₂O₃–Al₂O₃–SiO₂ in Phase Equilibria Diagrams*, CD-ROM Database, NIST Standard Reference Database, Version 4.1 (The American Ceramic Society, Westerville 2010), <https://www.nist.gov/srd/nist-standard-reference-database-31>
- 45.55 P.S. Danielson, M. Dejneka, A. Ellison, T.J. Kiczenki: Rare earth containing glass material and sub-

- strate and device comprising such substrate, Patent US8187715 (2012)
- 45.56 E. Downing, L. Hesselink, J. Ralson, R. Macfarlane: A three-color, solid-state, three-dimensional display, *Science* **273**, 1185 (1996)
 - 45.57 M. Dejneka: Transparent oxyfluoride glass ceramics, *MRS Bulletin* **23**, 57–62 (1998)
 - 45.58 M.J. Dejneka: The luminescence and structure of novel transparent oxyfluoride glass-ceramics, *J. Non-Cryst. Solids* **239**, 149–155 (1998)
 - 45.59 R. Silva: 3D TV is dead, <https://www.lifewire.com/why-3d-tv-died-4126776> (2017)
 - 45.60 K.P. Gadkaree, M.J. Dejneka, A.J. Ellison: Substrate compositions and methods for forming semiconductor on insulator devices, Patent US8530998B2 (2013)
 - 45.61 B.G. Aitken, M.J. Dejneka, K.P. Gadkaree, L.R. Pinckney: High strain glass/glass-ceramic containing semiconductor-on-insulator structures, Patent US7473969B2 (2009)
 - 45.62 K.P. Gadkaree, P.S. Danielson, M.J. Dejneka, J.C. Lapp, L.R. Pinckney: Germanium on glass and glass-ceramic structures, Patent US7456057B2 (2008)
 - 45.63 S. Garner: Introduction to flexible glass substrates. In: *Flexible Glass*, ed. by S. Garner (Wiley, Hoboken 2017) pp. 3–33
 - 45.64 Corning Glass Works: An electronic overcoat. In: *Sand and Imagination* (Corning Glass Works, Corning 1976) pp. 28–30
 - 45.65 Corning Incorporated: Corning® Willow® Glass, <http://www.corning.com/worldwide/en/innovation/corning-emerging-innovations/corning-willow-glass.html> (2017)
 - 45.66 M. Sato, N. Monozukuri: World's thinnest glass plate exhibited at show, http://techon.nikkeibp.co.jp/english/NEWS_EN/20141011/382042/?n_cid=nbptec_tecrs (2014)
 - 45.67 Corning Incorporated: Corning Lotus™ NXT glass chosen for Samsung display's flexible LTPS-OLED line, <http://www.corning.com/worldwide/en/about-us/news-events/news-releases/2017/05/corning-lotus-nxt-glass-chosen-for-samsung-displays-flexible-ltps-oled-line.html> (2017)
 - 45.68 S. Sisk, J. Koh, P. Su, B. Bowden: *Corning Lotus™ NXT Glass, Through its Advantaged and Balanced Glass Attributes, was Designed to Address the Challenges of Today's LTPS-OLED Manufacturing Processes*, Corning White Paper (Corning Inc, Corning 2016)
 - 45.69 OLED-Info.com: Flexible OLEDs: Introduction and market status, <https://www.oled-info.com/flexible-oled> (2017)
 - 45.70 K. Bourzac: Flexible glass could bring back the flip phone, <https://www.technologyreview.com/s/600894/flexible-glass-could-bring-back-the-flip-phone/> (2017)
 - 45.71 T.M. Gross, R. Youngman: Low modulus, damage resistant glass for ultra-thin applications. In: *Flexible Glass*, ed. by S. Garner (Wiley, Hoboken 2017) pp. 63–84
 - 45.72 digitimes.com: Flat panel demand to grow 7.2% in 2018, says IHS Markit, <https://www.digitimes.com/news/a20171123PR203.html> (2017)
 - 45.73 Corning Incorporated: A Day Made of Glass, https://www.youtube.com/watch?v=6Cf7IL_eZ38 (2011)
 - 45.74 Corning Incorporated: A Day Made of Glass 2: Same Day. Expanded, <https://www.youtube.com/watch?v=jZkHpNnXLB0&feature=youtu.be> (2012)
 - 45.75 A. Budholiya: Top trends in flat panel display market, TGDaily, <http://www.tgdaily.com/technology/top-trends-in-flat-panel-display-market> (2016)



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