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Glass Substrates for Liquid Crystal Displays

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We present a brief history of substrate glasses developed by Corning Incorporated (Corning) for use in Active matrix liquid crystal display (AMLCD) displays. The most basic attributes required of AMLCD substrates include thermal and mechanical stability, precise geometry control, a surface that is basically perfectly smooth, and no inclusions large enough to block a pixel in the final display. In addition, the glasses used as substrate materials must be essentially alkali-free so that they do not interact chemically or electronically with thin-film transistors (TFT). Thin, precision sheet was first made at Corning via the slot-draw process, but was eventually moved to the fusion-draw process; neither process was originally intended for this application. Alkali-free glasses were originally developed for electronic applications and lamp envelopes, and considerable research was required to invent compositions that were compatible with the high-viscosity fusion-draw process. Examples of the technical challenges presented by the evolving industry requirements are provided, including eliminating arsenic from the substrate glass and reducing the dimensional change during high-temperature processing of polysilicon-based TFT.

Introduction

Active matrix liquid crystal displays (AMLCDs) are ubiquitous features of modern life: digital watches, cellular telephones, mobile and desktop computer screens, and most recently large screen televisions are familiar examples of various forms of this technology. As interest in energy consumption by electronic devices becomes more important in the eyes of the consumer public, it is anticipated that CRT and plasma displays will gradually be replaced by AMLCD and organic light-emitting diode (OLED)-based devices.

What is less obvious is that each AMLCD uses two exquisitely engineered pieces of glass, the thin-film transistor (TFT) array backplane and the color filter (CF). The technology required to obtain large pieces of thin glass to the level of quality and geometric precision required for this application is truly astonishing, the more so given that it operates at a level of more than two billion square feet of glass per year. Furthermore, the glass itself is a unique material, specifically designed for the application. These glasses bear far more in common with laboratory glassware and—oddly enough—envelope glasses for halogen lamps than with the flat glass used in windows, containers, and windshields. Furthermore, much of the glass used in AMLC display technologies is produced via the fusion process, a unique process capable of producing what is essentially a precision ''fire-polished'' surface that requires no fur-

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ther modification (e.g., grinding or polishing) for use in this demanding application.

The intent of this paper is to outline the development of glass developed for AMLCD products at Corning Incorporated (Corning). The basic requirements for AMLCD substrates are described, followed by a history of the development of the fusion process, the alkali-free glasses used in AMLCD substrates, and a couple of case studies in AMLCD glass development. We close with a discussion of possible trends in AMLCD substrates. This is necessarily a one-sided, and regrettably, rather circumspect presentation; a great deal of the information about specific processes used is available in the form of patents, but much less is disclosed in peer-reviewed journals or in conference proceedings because of the highly proprietary nature of the information. Nevertheless, we hope to provide a view of the path by which these products came into being, and perhaps a view of where the path may take us in the future.

Basic Requirements for AMLCD Substrates

The two pieces of glass in an AMLCD device are the TFT backplane and the CF. Both are substrates, the first for the vapor-deposited silicon that forms the basis for the transistor array, the second for the CF materials that enable the RGB displays that we have come to expect from such devices. Between these sheets is a very thin layer of liquid crystal, often with supports to force the gap between the sheets to a very tight tolerance. The thickness of the gap and the registry between the pixels in the TFT array and the CF array are critical to the operation of the device. A quick glance at a modern AMLCD display will teach the reader that the pixels are exceptionally small and densely packed together, and although it is not obvious, each pixel is in fact three: a red, green, and blue element, each individually addressable. Therefore, precise registry between the CF and TFT backplane is essential to the most basic aspects of AMLCD device performance. The geometry requirements for both TFT and CF substrates are essentially the same, but the chemical requirements for the TFT substrate are more rigorous, and thus AMLCD panel manufacturers generally require that the same product specifications apply to both products. For this reason, most of the discussion that follows concerns the TFT backplane product.

From the vantage of the substrate provider, this leads to a number of product requirements for the substrate itself. Some of these are discussed by Dumbaugh and colleagues,[1–5] but are reviewed and expanded upon here in light of current product standards.

1. *The substrate must behave as a rigid solid through the entire range of processing conditions to which it will be exposed in TFT and CF manufacture*. Broadly speaking, TFTs come in two flavors. The largest volume of AMLCDs use amorphous silicon (a-Si) to make the TFTs. a-Si processes involve a low-temperature consolidation step that is typically $<350^{\circ}C$ for exposures times of 1 h or less. This is well below the annealing point for most commercial flat glasses, and were this the only requirement, then most commercial flat glasses might suffice for this application. If an a-Si layer is subjected to careful thermal cycling, it will substantially crystallize into small, subpixel-sized crystals, referred to as polysilicon (p-Si). p-Si displays are mostly found in hand-held devices, but are a basic requirement for OLED displays, and hence may represent the future for large, energy-efficient display devices. In the so-called "low-temperature" p-Si process, peak temperatures generally exceed $600^{\circ}C$ for periods of minutes to the better part of an hour, with some processes going well above $700^{\circ}C$. This approaches or exceeds the annealing points of most commercially available AMLCD substrates, and a specialized, very high-strain point glass such as Corning's Jade™ (Corning Incorporated, Corning, NY) substrate is required for these very demanding applications.

2. *The substrate must have an extremely precise, reproducible geometry*. There are many, many aspects of geometry, some of which have spawned new metrology methods simply to characterize the tiny deviations from a perfect, defect-free plane that is seen in AMLCD substrates. The product specification list varies from one customer to another, and thus to sell one product to many customers it becomes essential to simultaneously meet or exceed the most exacting customer specification for each attribute. A few key attributes include the following:

- Warp, or curvature out-of-plane through a moving window and across the entire sheet;
- 3-D Shape, or the large-scale distortion out-of-plane of the sheet, even when it is within warp specifications, for example, dome, hyperboloid, etc.;
- Wedge, or the variation in sheet thickness from one side to another, from center to edge, etc.

3. *The geometry of the sheet should change as little as possible during processing of the TFTs*. Geometry changes arise from several factors, the most important of which are stress induced across an entire sheet by the forming process,

what we will here call "fictive temperature reset," and thermal sag. Full sheet stress is subject to a very tight control, and for the most part can be addressed by careful thermal management in the sheet fabrication process. Fictive temperature reset arises from the fact that glasses never structurally equilibrate at the temperatures at which the sheets are subsequently processed. As a result, when the sheet is reheated—even at a much lower temperature—structural relaxation occurs on an atomic scale, resulting in an irreversible change in volume. In a-Si processes, the sense of the volume change is nearly always negative, and thus it is referred in the trade as "compaction." If all sheets from all suppliers compact identically, then panel makers would simply account for this in their processes. In fact, different sheets from different tanks or forming processes will have slightly different thermal histories, and thus will show slightly different magnitudes of compaction. It is this variability from one crate of glass to the next that is most important to control. The basic means to control this are either to introduce more of an anneal during the cooling of the glass so as to lower the fictive temperature, or to increase the annealing point of the glass so that the difference between it and the maximum processing temperature is as large as possible. Thermal sag is simply the viscoelastic response of a glass to a gravitational field. It is hard to manage gravity in a customer's process. Fortunately, in a-Si processing, temperatures are seldom high enough to produce measurable thermal sag, but this is not true for p-Si processes. We will discuss an example of addressing fictive temperature reset and thermal sag in the section concerning the development of Corning's low-T p-Si substrate, Jade™.

4. *The substrate must be as nearly as possible entirely free of surface perturbations that will interfere with cell gap spacing*. Obvious sources of surface defects are chips of glass produced during cutting of the ribbon or in subsequent edging operations, or dust particles that settle on the surface of the glass while it is still hot, welding in place. These can be surprisingly difficult to remove once present. If the thermal profile of the glass being pulled into sheet is not handled correctly, then larger scale bulging and necking within the sheet can occur that causes a larger-scale out-of-plane deviation. Compositional heterogeneity (known in the trade as "cord") can cause viscosity and refractive index variations that impact sheet thickness and, perhaps, transmission of light through the plane of the sheet. The most pernicious surface defects; however, are internal, within the bulk glass itself. Examples include devitrification products from free glass surfaces or orifices at or near the forming process, bubbles ("seeds" or "blisters") resulting from incomplete fining of the glass, and partially melted batch materials ("stones" or "knots") resulting from incomplete melting or inadequate homogenization. Cord and solid or gaseous defects can result from deficiencies in the melting process, but poor choices for raw materials, interactions between hot glass and the refractory or precious metal within the melting, conditioning and forming systems can play a very large role as well.

5. *The substrate must be as nearly as possible free of inclusions larger than about 1/4th of the area of a pixel*. The inclusions in question need not be opaque; any clear inclusion with a refractive index that contrasts with the bulk glass (e.g., a bubble or a melted, but not homogenized, sand grain) will bend light away from the normal to the display surface and result in a dim or dead pixel. The size indicated here is a rather arbitrary number, but gives a sense for the size of defects that we, as glass manufacturers, work very hard to avoid: a typical pixel in a AMLCD display is 50–100 μm in diameter, hence customers may be sensitive to defects 25–50 μm in diameter. It is a challenge even to inspect for defects so small, and thus large part of the focus of AMLCD composition and process R&D is aimed toward eliminating such defects altogether.

6. *The substrate should be durable enough to withstand the chemical treatments that it will experience during TFT manufacture, and likewise long-term exposure to normal environmental conditions in service*. The various cleaning and etching processes to which TFT and CF substrates are subjected can cause corrosion or heterogeneous etching of indurable glasses. The etch behavior of substrate glass is primarily an attribute of the bulk glass. The component that has the largest impact on relative etch rates is boron oxide, which is readily leached in mineral acids and which can result in the formation of a differentiated leached layer at the glass surface. High alkaline earth oxide concentrations in fluorine-rich etchants can also result in surface differentiation.

7. *The substrate should not interact chemically or electronically with the TFTs in their normal operation*. Aside from extrinsic contamination, for example, dirt, organics, etc., that can be handled in careful cleaning operations, the main source of chemical interactions between silicon and the underlying substrate is the mobile components in the glass itself. Whether sodium and other alkalis in soda-lime silicate glass can be handled by combinations of alkali leaching and/or barrier layers is a long-standing question in TFT panel manufacture. Sodium is definitely mobilized by an elevated temperature, and it is widely accepted that this interferes with the TFT performance. However, early

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research,[1] showed that even when initial contamination was avoided, cycling of the TFTs through large numbers of on–off cycles would produce sodium migration out of the glass even at an ambient temperature, although it appears that progress is being made on this front. For example, workers at Applied Materials Inc. published a method for producing high-temperature TFTs on soda–lime silicate glass involving a two-layer barrier layer comprising silicon oxynitride and a-Si.[6] Whether this will serve as a long-term solution to the problem of sodium migration remains to be seen.

Making Precision Flat Glass

The attributes discussed above divide neatly into two categories of challenges: Attributes 1 through 4 are most strongly impacted by the details of the melting, conditioning, and/or sheet-forming processes; attributes 5–7 arise at least in part—if not entirely—from the composition in the process. We consider first flat glass melting and forming processes at Corning, and the compositions used in these processes in the next section.

The question of how to make precision sheet from a stream of glass is a very old one. Cable[7] has provided an excellent review of many of these early approaches. Fascinating early patents regarding up-draw processes include those by Lubers[8,9] for preparing cylinders that were subsequently flattened into sheets, and by Fourcault[10,11] and Colburn[12,13] for direct up-draw of sheets from the surfaces of glass melts.

The world of flat glass changed dramatically with the introduction of industrial-scale float glass processes in the early 1960s. Today, nearly all of the flat glass produced worldwide is made via the float process or variants thereof. The fundamental elements of this process were first described in a patent by Pilkington and Bickerstaff.[14] (Edge[15] has an excellent review of the basic Pilkington approach and variants). A key development for specialty glasses was microfloat technology, which permitted the production of comparatively small volumes of high-quality glass via the float process, and an interesting review of its application and limitation is provided by Kloss *et al.*[16] This is the primary means by which Asahi Glass Company produces its flagship AMLCD substrate, AN100.

A great feature of the float process is that delivery of glass on hot tin metal and subsequent thermal management result in a partial anneal of the glass, and an anneal can be more or less obtained by adjusting the temperature profile and flow. Unfortunately, one surface contacts a tin batch, resulting in interesting surface features, and the other is exposed to an atmosphere comprising, among other things, particles of glass and partially oxidized tin that rain down on the glass surface. As a result, AMLCD glass produced by the microfloat process must be polished to a final thickness to remove such defects, and the polishing itself can introduce new defects to the surface resulting from dig and gouge from the polishing media.

Slot Draw: A Down-Draw Process

In the mid 1940s, Brown at Corning filed a patent for a very different approach, a down-draw process in which glass was delivered into an elongate conditioning system and removed via a carefully machined slot in its bottom.[17] A figure from Brown's patent is shown in Fig. 1. Tractors grabbed the glass sheet and pulled into either straight down to be cut off (as described in the original patent) or through a 90° curve into an annealing lehr. This approach came to be described as slot draw. Subsequent developments provided improvements in edge-to-edge thickness control, and eventually a particular glass, Corning 0211, was produced in very thin sheets for use as covers for microscope slides. Other glasses were manufactured in small

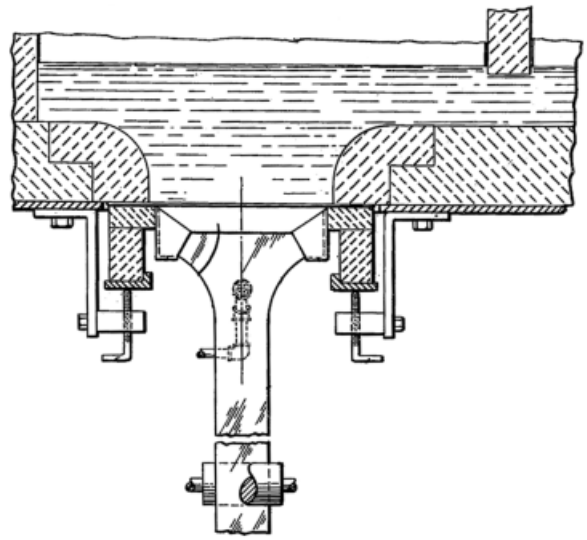


Fig. 1. The slot draw-forming apparatus as envisioned by Brown.[17] The molten glass collects in a receptacle above the slot. The shape of the slot keeps the glass from becoming too thin at the edges by supplying additional glass at an angle with respect to the pull direction. The continuous glass ribbon is pulled by pulling rolls, and can be cut to size or passed through an annealer below the rolls.

volumes via the slot draw approach, and in the early 1980s, Code 0211 was sold as Corning's first offering as an LCD substrate.

Slot draw has the advantage that it provides what is essentially a fire-polished surface that—if the sheet geometry was acceptable—needs no further treatment before use; however, it became clear that there were several deficiencies as well. Chief among these were that the orifice needed to be machined to very high tolerances to produce a precision sheet, that condensation and devitrification around the slot orifice showed up as surface defects and sometimes perturbations to the sheet shape itself (hence requiring cessation of operations to clean up), and that even with comparatively low-temperature glasses, it was very difficult to maintain the precision geometry of the slot over extended periods of time. Other aspects of control of sheet shape were in their infancy at the time, and it is clear now that improvements to heat management around the orifice and environment management around the forming process would produce much improved surface quality and sheet geometry. Schott Corporation currently uses a variant of the slot draw technique to make very thin AM-LCD display-type glass for mobile applications.[18]

Fusion

In the early 1960s, Corning engineers Stuart Dockerty and Clint Shay proposed a radically different approach to obtain sheet via a down-draw process.[19] Glass was introduced into a tube with a teardrop-shaped cross section with a slot across its upper (rather than lower) surface. Glass overflowed this forming mandrel to either side, and the two glass streams joined or "fused" at the pointed end of the teardrop. This joining of two glass streams along a tip became known as the "fusion" process. Unlike any previous sheet-forming process, the forming surfaces that contact the glass were interior to the sheet: in the up-draw processes and slot down-draw processes, the glass contacts the orifice of the forming slot, and in the float process one surface contacts a tin bath. The surfaces of the glass that were in contact with the forming surface were thus buried within the sheet, and the exterior surfaces of the glass sheet were contact-free.

Later, Dockerty[20] proposed an improved fusion process, wherein glass was poured into a trough and overflowed its walls (Fig. 2a and b). The molten glass flows over converging forming surfaces below, and the separate flows fuse the tip, or root, to form a continuous ribbon of glass. The forming mandrel used in this process has become known as an "isopipe," where "iso" refers to the notion that there is a uniform rate of flow of glass out of the trough and over the weir walls along the entire length of the trough. The combined force of gravity and tension and the speed of pulling rolls at the edges of the sheet were used to make the sheet thicker or thinner. As the glass ribbon descends from the

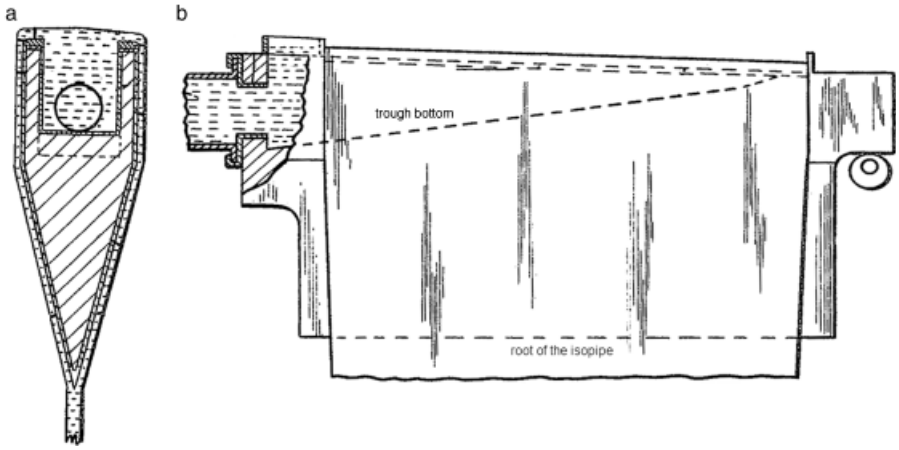


Fig. 2. (a) A cut-away drawing of an isopipe, the forming anvil used in the fusion draw process.[20] The diagonal lines indicate the refractory, and the horizontal dotted lines represent glass. The refractory trough at the top of the figure is defined by the weir walls. Glass overflows the weirs, flows down either side of the refractory, and joins at the base, or root. (b) The isopipe is seen perpendicular to the face of a sheet. The dashed line near the bottom represents the root, or base of the refractory. The trough (diagonal dash line increasing from left to right) is deeper at the left (inlet) than at the right to ensure uniform glass flow over the walls of the trough.

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root of the isopipe, it cools through the glass transition temperature and becomes an elastic ribbon, at which point it can be cut to form smaller sheets of glass. In broad strokes, the above discussion is the essence of the fusion process as it is practiced today.

Modeling calculations performed by Dockerty showed that a thin precision sheet would require pulling glass off the bottom (or root) of the forming mandrel (or isopipe) at very high viscosity, on the order of 10^4–10^5 Pa s. By contrast, the float process typically delivers glass at a viscosity of about 10^3 Pa s, and slot draws are typically operated at 3000–5000 Pa s. This has implications for the types of glasses that can be made into thin precision sheet, as is discussed below.

Fusion was used originally to make glass intended for the automobile windshield market, although this was abandoned after a tepid response from potential customers.[21,22] In the mid 1970s, fusion was used to make sheets of photosensitive glass that were later sagged under gravity to obtain near-final-form products for customers.[21,22] It was from such a tank that the first fusion-drawn LCD substrates were made.

Evolution of Corning's Glasses for Liquid Crystal Displays

Corning has sold many glasses for electronic applications of one form or another, but a much more limited set has been proposed or sold specifically for TFT applications. The first and longest running flat glass made by Corning using the slot-draw process was Code 0211, an alkali zinc borosilicate (Table I). Although originally intended primarily as ultrathin microsheet glass, it was nevertheless used in the earliest stages of investigation of thin-film tranisitors,[23] and for some time was a typical substrate used in early LCD devices, particularly watches and clock displays. Its main attractions early on were that it was available as very thin sheet, and that its sodium content was typically well below that of conventional soda-lime silicate glass.

Code 7059: The First Alkali-Free AMLCD Substrate

By the early 1980s, it was apparent that the sodium content of Code 0211, while not high, was nevertheless a problem for TFT device lifetime,[1] and a large effort was undertaken at Corning to identify possible replacements. Corning sent samples of Code 7740 Pyrex™ (Corning Incorporated) to customers to evaluate in TFT applications. It had a much lower coefficient of thermal expansion (CTE) and about half of the sodium of Code 0211, and was believed to be compatible with the fusion process as practiced at that time. However, though alkali mobility was much reduced—and device lifetime correspondingly enhanced—it was not zero.[1] This led to a search at Corning for alkali-free glasses to replace Code 0211.

That alkali-free glasses would work better than alkali-containing glasses was not a new idea: Alpha and

Table I. Compositions of Corning Glasses Proposed or Sold for use as LCD Substrates

Code	Description	Strain Pt. (°C)	CTE ($\times 10^{-7}$/°C)	Density (g/cm^3)	Year sold (developed)	Reference
0211	Alkali zinc borosilicate	508	74	2.53	1953	First LCD product
7740	Alkali borosilicate	510	32.5	2.23	1933	Sampled (1982*)
1724	Alkaline earth borosilicate	675	43.5	2.64	1981	Z
7059	Barium borosilicate	595	46.7	2.76	1956	First alkali-free
1733	Alkaline earth borosilicate	643	36	2.48	1990	Zz
1734	Alkaline earth borosilicate	661	48	2.70	1992	Zzz
1735	Alkaline earth borosilicate	665	49	2.70	1992	Zzzz
1737	Alkaline earth borosilicate	666	37.8	2.54	1993	
1737G	As-free alkaline earth borosilicate	668	36.7	2.54	1997	Third LCD product
Eagle^{2000}™	Alkaline earth borosilicate	666	31.8	2.38	2000	Fifth LCD product
Eagle XG™	Alkaline earth borosilicate	669	32	2.38	2006	Sixth LCD product
Jade™	Alkaline earth borosilicate	740	37.5	2.63	2008	Low-T p-Si product

*Invented in 1934, commercial product for many years. Sampled to customers as thin sheet for use as an LCD substrate in 1982.

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Dumbaugh[24] recognized in the mid-1970s that an alkali-free glass would be desirable for TFT applications, and proposed alkaline earth borosilicates. Among the attributes cited by Alpha and Dumbaugh that made such materials well-suited for this application were that they are substantially free of alkalis, have CTEs that are more like that of silicon than is the case for soda-lime silicate glass, and that their strain points can be quite high, which in turn permits higher processing temperatures for better device performance. Corning had long sold a glass used in resistors, Code 1723 (later to become an envelope glass for tungsten–halogen lamps), and glasses similar to 1723 are listed in their patent.

The first alkali-free glass sold specifically for TFT applications was Corning Code 7059, also one of the first alkaline earth borosilicate glasses produced explicitly for any electronic application. Code 7059 was invented in the late 1950s by a Corning scientist George Hares, with the intended application of being used in resistors. Over the years, it was made into sheet via slot draw for various customers, and it was in this form that it was first provided to potential TFT customers. A trial was conducted in the early 1980s to see whether it was compatible with the fusion process as then practiced, and when a good result was obtained, it was moved into manufacturing.

As with other borosilicates sold by Corning, Code 7059 was classified as a "Pyrex," albeit an alkali-free pyrex with a low alkali content. Its properties are listed in Table I. Compared with modern display substrates, its CTE and density are quite high and its annealing point is quite low, but the annealing point and CTE in particular were seen as very attractive at the time. Liquid crystal display technology appeared to be at a cross road then, either moving toward less efficient, lower resolution a-Si devices, or more efficient, higher resolution thermally processed p-Si. As noted above, the lower temperature processing of a-Si devices appeared to allow for a lower temperature substrate, thus Code 7059 and competitor products like it quickly caught on for AMLCD applications.

Toward High T_g Glasses: Code 1737and Eagle$^{2000™}$

One troubling feature of Code 7059, and indeed of any glass with a glass transition temperature close to the peak temperature in a process, is fictive temperature reset (discussed above). Rather than the glass transition, most in the industry refer instead to properties that can be measured via standard viscometry methods, the annealing point at about $10^{12.2}$ Pa s, or the strain point at about $10^{13.2}$ Pa s (see Appendix A). At the much higher temperatures associated with thermal annealing of p-Si, the compaction can be quite large, and can depend sensitively on the thermal history.[25] The TFT and CF substrates experience quite different thermal histories: TFT substrates are typically held at 300–350°C for a period of tens of minutes to anneal the a-Si thin film, but peak CF processing temperatures are about 200°C. The TFT processing temperature is closer to T_g, and thus TFT substrates show a small but important change in dimensions relative to CF substrates made from the very same glass. This can result in a failure of registry between the CF and TFT arrays, resulting in permanently bright or dark areas in an assembled display.

Some level of fictive temperature reset is inevitable for all but dead-annealed glass, but it is more acute for non-contact sheet forming processes like slot draw and fusion draw. This is because the sheet descends from the forming slot or mandrel in air, cooling very rapidly and producing high-fictive temperature. The rate of cooling can be slowed by putting heating elements around the descending sheet, but at some point it must be scribed and broken off for inspection and packing, and completely relaxing the glass to its anneal point, for example, would require many hours at the anneal point, not the tens of seconds available in a fusion-draw machine. A limited anneal occurs in the float process as the molten glass is transported along the tin bath and out for cutting, but capacity limits how well annealed the final sheet can be. In either case, the fictive temperature of the glass produced during its manufacture is invariably higher than the peak temperature used in the subsequent processing. While it might seem reasonable to impose a secondary anneal on a sheet after it is fabricated, in practice this is fraught with difficulty, not only because of the long time at high temperature required to produce the anneal but also because particles readily stick to hot glass, thus compromising its untouched surface.

It was apparent early on that fusion-drawn Code 7059 demonstrated non-negligible fictive temperature reset not only in p-Si processing but also on a much smaller scale in a-Si processing. As noted earlier, the peak processing temperature in these processes tend to vary over a narrow range and the panel manufacturers' need for throughput dictates that the time spent at high temperature should be as short as possible to obtain the desired performance from the TFT array. Thus at the

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time, it was not obvious that this represented a long-term problem.

It happened that alkali-free glass compositions were also highly desired for emerging applications in tungsten–halogen lamps and molybdenum-sealing glasses. The CTEs required for these applications were similar to that of Code 7059: around 45×10^{-7}/°C for tungsten halogen lamp envelopes,[26–29] and about 50×10^{-7}/°C for molybdenum sealing glasses.[30,31] The strain points required were high as well to avoid deformation at the higher temperatures obtained during lamp operation. The combination of high-strain point and suitable CTE made such materials logical starting points from which to develop new TFT substrate compositions.

In anticipation of the day when this problem might become more important for a-Si applications, a group of Corning scientists led by Dumbaugh at Corning Inc. set about trying to create a high-temperature alkali-free glass that was compatible with the fusion process. Two glasses based on the earlier lamp envelope glasses were evaluated for use as substrates in p-Si TFT devices, Code 1735 and Code 1734, in the order of an increasing strain point.[32] Unfortunately, a development trial of Code 1735 on a fusion draw revealed a tendency to devitrify on the isopipe. The root problem was the comparatively high-liquidus temperatures of these glasses. When superimposed on their viscosity curves, the temperatures translated to relatively low liquidus viscosities. Recall from above that Dockerty had already determined that high viscosities were required for thin, precision sheet via the fusion process. Using the technology available at the time, it was found that at viscosities that permitted the formation of high-quality sheet, the glasses were unstable and would form devitrification products that in turn would show up as pixel-blocking inclusions in the glass. On the other hand, at viscosities such that the devitrification was reduced or eliminated, it proved impossible at the time to produce high-quality sheet. The terms "fusion-compatible" and "high liquidus viscosity" quickly became linked in Corning R&D. In addition to sending the composition team back to the drawing board, the Code 1735 experience prompted work to develop newer and more reliable methods to determine liquidus temperature (see Appendix A).

The composition team undertook to identify at least one alkaline earth borosilicate with a liquidus viscosity of about 10^5 Pa s. Dumbaugh and his team melted and characterized over 10,000 glasses from the late 1980s through the early 1990s in the quest for high-strain point, fusion-compatible glasses.[33–40] Code 1733[2] was an early result of this work, but proved difficult to form, perhaps because of a weak tendency to phase separate into two liquids at draw temperatures. The developmental glass Code 1729 also came out of this work. Code 1729 is an ultrahigh strain point glass aimed squarely at thermally processed p-Si. It was shown to represent exciting possibilities for high-temperature processing of p-Si thin films,[41] but an in-house analysis concluded that it would be exceptionally difficult to manufacture, and thusfurther development was halted.

The ultimate result of this investigation[42–45] was Code 1737, which eventually became the flagship TFT substrate product for a-Si applications.[46,47] The basic properties of Code 1737 are shown in Table I. It achieved the basic requirement of increasing the strain point enough to mitigate against fictive temperature reset in a-Si processing, but it also provided a liquidus viscosity in excess of 10^5 Pa s, which ensured that it could be made into precision sheet via the fusion process.

Code 1737 is an interesting study of the response of an emerging market to a new material. It was primarily intended to be a bridge material between a-Si and p-Si applications that leveraged the fusion process to make thin, precision sheet. From the vantage point of customers; however, it had other very desirable attributes. Its CTE was the lowest of any TFT substrate glass available at the time, and a much better match for the CTE of a-Si itself. It also had a much lower density than any competing glass, which was considered very desirable for the emerging market in mobile computers. By design, its high-strain point resulted in a much lower fictive temperature reset during a-Si processing. These attributes generated nearly instant market pull for the new glass, and in its arsenic- (1737) or antimony-fined (1737G) incarnations, Code 1737 was sold for 10 years, the longest run for any AMLCD product sold by Corning.

If customers liked the lower CTE and density of Code 1737 compared with its predecessor, Code 7059, it appeared reasonable that further decreases in both would be welcome. This appeared particularly salient given the increasing popularity of laptop computers and the growth of their share in the overall AMLCD market. In an era of lightweight, high-performance notebook computers, it can be hard to remember that at one time, weight trumped nearly all attributes in the minds of laptop computer customers. Any steps that could be taken to shave grams of weight from devices were embraced by computer manufacturers, and this included the weight associated with the AMLCD display.

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Customer queries confirmed that a less dense, lower CTE substrate would have value, so in 1998 a new research team was constituted to identify a new substrate glass with substantially the same strain point as Code 1737, but still lower CTE and density.

In truth, exploratory research to understand composition trends in alkali-free borosilicate glasses had never ceased. It is said that experience is recognizing a problem when it is experienced again, and the challenges to be overcome in developing Code 1737 had prompted ongoing research to understand property–composition relationships in alkaline earth boroaluminosilicate glasses. Accurate empirical models to predict basic properties were already in hand, and much had been carried out to understand liquidus trends in these complex systems. As a result of this head start, it "only" required exhaustive characterization of about 1000 glasses to come up with a number of interesting possibilities.[48–52] The final selection ultimately became the product Eagle$^{2000™}$ (Corning Incorporated), the lowest density, lowest CTE AMLCD substrate on the market (Table I), and unrivaled today by any commercial product except Eagle XG™. Eagle^{2000} was first introduced in 2000 and became Corning's primary AMLCD product by 2004.

The Problem with Arsenic: 1737G and Eagle XG™

From its inception, the RD&E scientists supporting the Advanced Display Products Division (eventually to become Display Technologies) were keenly aware that defects needed to be managed at all costs. The name of the game in TFT manufacture is throughput, and thus Corning's customers build larger and larger fabrication lines capable of putting more displays of increasing size on a single enormous sheet of glass. Unfortunately, panel manufacturers typically find pixel-blocking defects after the entire display is assembled, in the form of a dead pixel: this is a very late stage in which to discover that the substrate glass contained a defect.

The most pernicious defect in any substrate glass is bubbles, sometimes referred to as seeds or blisters. Some of the batch materials that go into a display of borosilicate glass—particularly alkaline-earth carbonates, boric acid (the usual source material for B_2O_3)—produce prodigious volumes of gas per unit weight. Furthermore, the glasses are generally melted with the assistance of gas burners, which add similarly huge amounts of carbon dioxide and water to the air space above the glass surface. Air and nitrate batch materials (if used) also contribute nitrogen to both the cover gas and to the porous batch materials as they melt down into glass. Therefore, the glass contains substantial amounts of dissolved water, carbon dioxide, and nitrogen. Preexisting bubbles containing CO_2 and N_2 in particular tend to shrink as per the ideal gas law, but unless they are very small to being with, they do not entirely disappear without assistance.

Stokes Fining and Chemical Fining Agents

The two methods widely used in glass manufacture to eliminate bubbles are to incorporate a finer (sometimes called a refiner) in the melt system, and to add a chemical fining agent. A finer is a section downstream of the melter in which the glass has a clean free-air surface. The hope is that gas bubbles already in the bulk glass can rise up to the surface and pop, clearing them from the glass stream. Generally, the depth of glass is kept low and its flow condition largely laminar. The density contrast between the bubble and surrounding glass is enormous, and for all intents and purposes the density of the gas in the bubble can be ignored. For typical fining viscosities of 10–50 Pa s, and maximum flow velocities on the order of 0.1 m/s, the Reynolds number is on the order of one or less, and thus a simplified form of the Stoke's Law can be used to estimate the terminal velocity, v_t, of a rising bubble[53]:

$$v_t \approx \frac{2}{9}\frac{gr^2\rho}{\eta}$$

where g is the acceleration due to gravity, r is the diameter of the bubble, ρ is the glass density, and η is the glass viscosity. For bubbles on the order of 50 μm, a glass density of 2.5 g/cm^3, and a viscosity of 10 Pa s, the terminal velocity is on the order of 10^{-3} cm/s, and such a bubble ought to be quite close to the glass–air interface if there is to be any hope of keeping it from appearing in the final ware.

This leaves the glass manufacturer with two options: lower the viscosity of the glass, or increase the size of the bubble. A 10-fold decrease in viscosity will increase the bubble rise velocity 10 ×, and in a residence time of about 30 min, a small bubble might move through 2–3 cm of glass. Increasing the temperature to produce this viscosity change will also expand the size of the bubble via the ideal gas law. Unfortunately, AMLCD substrate glasses sold today are very "hard" glasses, meaning that they melt at very high temperatures; the

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temperatures corresponding to 10 Pa s are very typically 1700–1800°C, and to decrease this to 1 Pa s would require temperatures well in excess of 2000°C. This would produce only about 20% increase in bubble volume, and would represent a stunning level of pain for a comparatively modest gain.

It remains, then, to increase the size of the bubble, and this is accomplished with a chemical fining agent. For many years, glass manufacturers have deliberately added components that decompose at high temperatures, releasing gas into existing bubbles. Sulfate fining is very commonly used in the manufacture of soda-lime silicate glass, but has generally proved vexing for alkaline-earth borosilicate glasses due to their tendency to retain dissolved sulfate to very high temperatures. For these much harder glasses, the preferred approach for many years has been to add a multivalent oxide, particularly oxides or arsenic or antimony. In whatever form these oxides are added, they experience an initial oxidation step as the batch heats up, with arsenic partially or entirely converting to As_2O_5 or arsenate salts, and antimony converting partially or entirely to cervantite, $Sb^{III}Sb^{V}O_2$. As these compounds continue to heat up and dissolve into the glass melt, they decompose back to trivalent states, nominally As_2O_3 or Sb_2O_3:

$$As_2O_5 \rightarrow As_2O_3 + O_2$$

This process liberates oxygen, but since the only multivalent in the glass was the source of the oxygen, it very quickly exceeds 1 bar in pressure and leaks into existing bubbles. Because the absolute volume of pre-existing bubbles is very small, thus the total amount of arsenic dissolved in the glass that must be reduced from the +5 to 3+ valence state is typically quite small. For example, if a glass melt contains 10,000 bubbles/L that are on the order of 100 μm in diameter, the oxygen generated by the decomposition of about 0.01 wt% of As_2O_5 entirely to As_2O_3 is sufficient to increase their volumes by 10 ×.

Unfortunately, much of the arsenic added to the batch reduces at much lower temperature. Of the oxidized arsenic ions that remain, many will be too far from bubbles to contribute oxygen to them. Therefore, arsenic oxide is typically batched at a level of 0.2–1.2 wt%, depending on the glass and the melting process, with higher levels used more often than not as insurance against upsets. Antimony oxide is almost entirely reduced, and therefore is much less effective as a fining agent; antimony oxide levels of 1–2 wt% are very typically used to obtain substrate-quality glass in these systems.

Eliminating Arsenic: Development of Code 1737G

In the United States, the Resources Conservation and Recover Act defines arsenic as a heavy metal, and its levels in waste streams is subject to strict control by the U.S. Environmental Protection Agency, and often still stricter laws and regulations within various states. The rules governing whether the wastes containing arsenic are, in turn, hazardous are complex, but at their basis is a standard test called the Toxicity Characteristic Leaching Procedure, or TCLP.[54] In essence, a crushed sample of solid waste is held in a buffered aqueous solution for 24 h and the levels of heavy metals released to the solution are measured. If below the limits established by the EPA, the waste stream is considered nonhazardous. In this sense, if one wished to sequester arsenic so that it could do no more harm, one would be hard pressed to improve on AMLCD display glasses as hosts for this heavy metal, as the levels released in the TCLP test are typically orders of magnitude below the allowed values for nonhazardous waste. Outside of the United States; however, controls are often more stringent, and the absolute amount of arsenic in a waste stream is often subject to very tight control, regardless of whether the arsenic could be easily released into the environment.

Anticipating the need for customers to eliminate arsenic from their waste streams, a major effort was begun in 1994 to eliminate arsenic from Corning display substrates. After several other approaches proved difficult to implement, it was decided to focus on using antimony oxide as a fining agent. Antimony oxide is not subject to the same strict regulations as arsenic oxide, and would allow Corning's customers to continue to use Corning products in their processes. However, it is a very poor fining agent at high temperature because it is much more easily reduced than arsenic oxide. Because much of the volume of Corning display products had shifted from the lower-melting Code 7059 to Code 1737, the challenges associated with getting gas out of the glass were exacerbated by high-melting temperatures.

In the end, it took a combination of carefully selected raw materials, melt system modifications, the combined impact of antimony and chlorine,[55] and adjustments to the base composition itself to come up with an arsenic-free glass equivalent to Code 1737 in all its physical properties, including very low levels of gaseous defects. The new product, Code 1737G, was commercially announced in December 1996, and was manufactured until 2006.

Eagle XG™: Arsenic- and Antimony-Free Eagle Substrate

1737G was a success in that it allowed display panel manufacturers to take advantage of fusion-drawn glass but avoid regulatory challenges created by arsenic in the glass. However, in some jurisdictions the hazards associated with antimony are considered ''of a kind'' with arsenic, so considerable effort continued to identify composition and process approaches to eliminate antimony from Corning AMLCD substrate products. In particular, once Eagle$^{2000™}$ was commercially released, several panel manufacturers expressed interest in an arsenic-free version of this substrate. The melting temperature of Eagle^{2000} had pushed melting systems technologies to their limit, thus to keep gaseous defects to a minimum it was introduced as an arsenic-fined glass. Unfortunately, certain panel manufacturers quite literally could not use it in their devices due to local environmental and industrial regulations, and hence the quest for an arsenic-free glass with the properties of Eagle$^{2000™}$ started immediately.

It has been known for many years that tin (IV) oxide (SnO_2) works as a fining agent in the right glasses and in the right melting systems.[55] Tin has none of the hazards associated with arsenic or antimony. SnO_2 is a pretty good refractory, and in fact has been used in glass melting as an electrode material for many years.[56] It is not incorporated into the glass melt except at quite high temperature. As a result, its subsequent reduction releasing oxygen occurs at a late stage in melting—the very point at which the few remaining very small bubbles need to be removed—thus in this sense, it is very appropriate for high-temperature glass melting.

Unfortunately, the solubility of SnO_2 is a very steep function of temperature, and this presents a risk for the devitrification downstream of the melter. Once melting has occurred at a very high temperature, the remainder of the melt system between the melter or finer and the forming system is intended by and large to carefully remove heat from the glass. As noted above, the fusion process is performed at high viscosity, hence low temperature, and hence the glass temperature must be reduced several hundred degrees from its peak before it is delivered to the fusion machine. The solubility of SnO_2 decreases precipitously through this temperature decrease, and thus to keep cassiterite from appearing on the forming mandrel, it is important to keep its bulk concentration to a few tenths of a percent by weight.[57] Given the high levels of arsenic or antimony oxide required to obtain good fining, it is not too surprising that low levels of SnO_2 do not immediately result in high-quality glass.

Lab studies suggested that a combination of SnO_2 and a halide, coupled with a careful redox control of the glass in the early stages of melting, would yield good quality glass, but development trials showed that gaseous inclusions were not completely eliminated. Furthermore, the notion of incorporating halides into the glass appeared worth avoiding if possible, as most of the halogen batched comes out in the off-gas products from the melter. Experience with 1737G showed that halide release had a very deleterious impact on structural steel components, and significantly reduced the lifetime of key plant pollution control equipment.

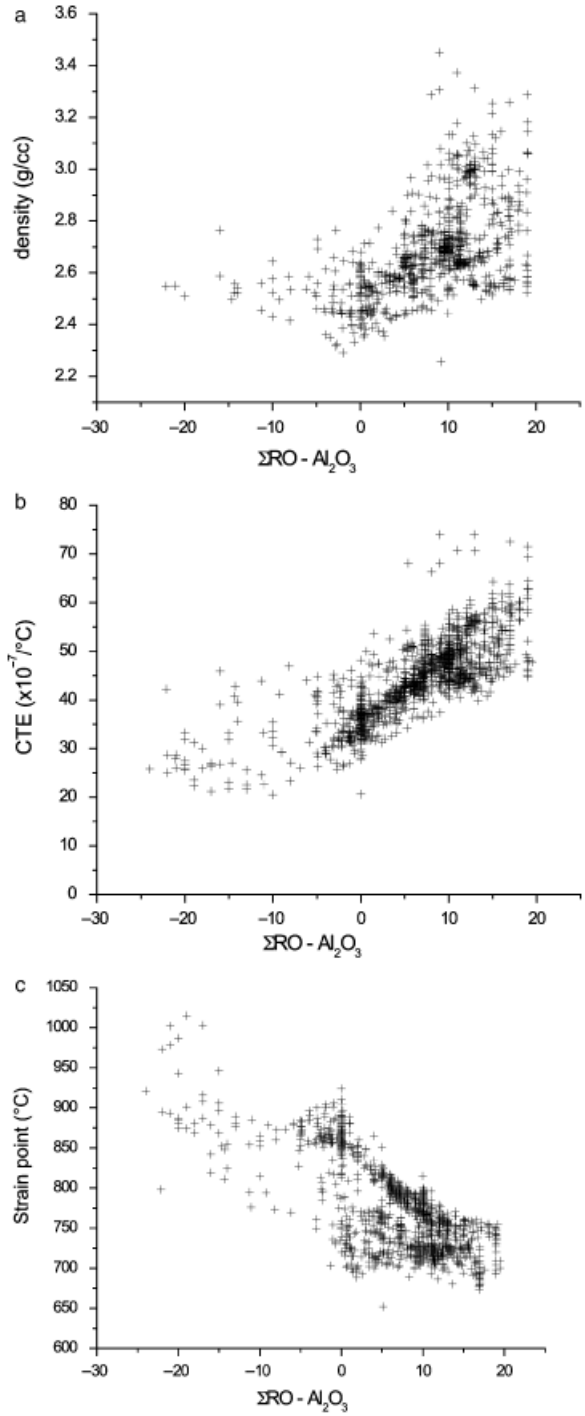
Separately, one of us (Ellison) had noticed a puzzling trend in laboratory melts of alkaline earth borosilicate glasses: when the moles of alkaline earth oxides exceeded the moles of aluminum oxide ($\Sigma RO–Al_2O_3 < 0$), the bubble density of the glass was invariably higher than when $\Sigma RO–Al_2O_3 > 0$, even when the glasses were melted at an equivalent viscosity. Unfortunately, other glass attributes are negatively impacted by increasing alkaline earth oxides. Figures 3(a) and (b) show density (3a) and CTE (3b) versus $\Sigma RO–Al_2O_3$ for a set of 1600 alkaline earth boroaluminosilicate glasses. As alkaline earth concentration increases, both density and CTE increase, a trend that is still more obvious if B_2O_3 and/or SiO_2 is held constant. Most of the spread in the two plots is due to the specific identity of the alkaline earths; large, heavy barium contributes much more strongly to both CTE and density than small, light magnesium, with calcium and strontium having intermediate impacts. Figure 3(c) is a plot of strain point for glasses in the same database versus $\Sigma RO–Al_2O_3$. Boron oxide also has a substantial impact on the strain point, and varies through a substantial range for the glasses in Fig. 3(c); yet, there is still a very strong trend of decreasing the strain point with $\Sigma RO–Al_2O_3$. Melting temperature (e.g., the temperature corresponding to a viscosity of 20 Pa s) follows a very similar trend.

From above, low density, low CTE, and high strain point were the key product attributes for Eagle^{2000}. As noted above, large alkaline earths tend to produce higher CTEs and densities, and lower strain points, than smaller alkaline earths, and likewise serve to increase melting temperature, and hence at first blush the answer would appear to be to replace large alkaline earths with small ones. Unfortunately, there is only a small amount of

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strontium and no barium in Eagle[2000], thus the size of substitution that can be performed is quite limited.

Furthermore, replacing a large alkaline earth element with a smaller one tends to increase the liquidus temperature, although the relationship is stunningly complex, particularly for $\Sigma RO–Al_2O_3$ close to 0.0. Thus, removing barium and replacing it mole-for-mole with magnesium reduces density and CTE, increases strain point, and lowers the melting temperature, but it lowers most of the viscosity curve between the melting point and strain point as well, and thus lowers the temperature at which glass is delivered and formed in the fusion-draw system. At the same time, it generally increases the liquidus temperature of the glass, and hence the liquidus viscosity decreases sharply if no other steps are taken.



The second composition discovery, then, was that by juggling the relative proportions of the alkaline earths relative not just to each other, but to SiO_2 and Al_2O_3 as well, it was possible to retain a liquidus viscosity high enough to ensure a good performance in the fusion process, yet also increase $\Sigma RO–Al_2O_3$ to a value comfortably in excess of 0.[57] Because the initial bubble concentration in the melt stage was lower than for Eagle[2000], the impact of the small amount of SnO_2 fining agent was greatly enhanced. When combined with other improvements in the melting process itself, it proved possible to obtain AMLCD-quality glass without arsenic, antimony, or barium, and while maintaining the extraordinary properties of Eagle[2000]. Eagle XG™ was announced in March 2006, and at the time of this writing, it is the flagship product for Corning Display Technologies.

What About p-Si? The Development of Jade™ p-Si Substrate

As noted above, much of the impetus to move from the comparatively low strain point Code 7059 to the much higher strain point Code 1737 was to facilitate thermally processed p-Si applications and products, and indeed developmental glasses with strain points like that of 1737 were shown to perform better than Code 7059 in thermally annealed p-Si applications.[58] Unlike the

Fig. 3. (a) Density (g/cm^3) versus $\Sigma RO–Al_2O_3$ for alkaline earth borosilicate glasses, in which ΣRO represents the sum of the mole percents of the alkaline earth oxides (MgO, CaO, SrO, and BaO). ΣRO ranges from from 0 to 20 mol%, B_2O_3 from 0 to 18 mol%, SiO_2 from 50 to 80 mol%, and Al_2O_3 from 4 to 34 mol%. (b) Coefficient of thermal expansion (RT-300°C) versus $\Sigma RO–Al_2O_3$ for the alkaline earth borosilicate glasses referenced in (a) (c) Strain point versus $\Sigma RO–Al_2O_3$ for the alkaline earth borosilicate glasses referenced in (a).

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float process, which delivers glass on a hot molten metal and keeps it hot through an extended period of time, fusion delivers glass directly into air, and while the thermal profile to the cut-off point can be managed to a considerable degree, unless one were to build a very tall fusion draw and stack a very tall annealer beneath it, fusion-drawn glass will inevitably have a higher fictive temperature than the same glass made via the float process. In fact, managing the thermal profile below the isopipe has proved critical to delivering ware that shows acceptable fictive temperature reset for a-Si processes.

Unfortunately, the thermal reset of as-drawn Code 1737 at temperatures appropriate for the thermal processing of p-Si TFT arrays proved too large for some customers, and thus for several years as-drawn sheet was subjected to a secondary annealing step to minimize thermal reset in low-temperature p-Si processing.[59] Unfortunately, this put the very properties intrinsic to the fusion process—excellent geometry and a fire-polished surface—in jeopardy; the sheet may warp or sag, and surface defects (particularly adhered glass particles and scratches) may be introduced while at the temperature within the annealer. One way to surmount the surface imperfections introduced by annealing is to polish the glass after annealing, but this then compromises the smoothness of the fusion-drawn surface.

Extensive research in this topic showed that fictive temperature reset was sensitively dependent on both thermal history and on the difference between the strain point and the highest processing temperature seen in the TFT application.[25,32] For a-Si processes involving temperatures of 300–400°C for exposure periods of 1 h or less, suitably low compaction can be obtained from an as-drawn sheet of a glass with a strain point of about 660°C, provided, of course, that this can be enhanced by managing the details of its cooling curve on the draw. As the annealing point increases, the thermal reset diminishes as well, as does the magnitude of variation in the thermal reset from one draw process to another.

Translating this result directly to p-Si would suggest a proportionate increase in strain point to surmount fictive temperature reset at elevated processing temperatures. However, it is much more complex than this. To keep processing temperatures as low as possible, p-Si process cycles tend to involve multiple cycles of heating and cooling, and at each stage the glass struggles to equilibrate to the new temperature. Some steps may produce substantial fictive temperature reset relative to the original-draw conditions, only to have this newly imposed fictive temperature reset itself in a subsequent step. When these steps occur before the final creation of the array of transistors, then they are of no consequence to the final product, but when they occur during or after creation of the array of TFTs, then there may be mismatch between the array and the CF. This shows up after the entire panel is assembled, and thus is a very late and expensive point to discover that a newly made panel is unusable.

The key to surviving such a process with the original dimensions largely intact is rather brute force: increase the strain point so much that in all low-temperature process steps, the extrapolated viscosity of the glass is very high. In this way, subsequent thermal processing produces much smaller absolute dimensional changes, and the resulting ware coming out of the process looks much as it did going in. This was recognized very early on by Dumbaugh and colleagues at Corning, and numerous patents were filed for very high strain point aluminosilicate glasses specifically intended for this kind of thermal processing,[33–40] and to the limited testing of the 800°C strain point developmental glass, Code 1729.[41] The main challenge with any of these compositions was to figure out how to make the glasses compatible with the existing melting and forming platforms.

A multidisciplinary effort was undertaken at Corning Inc. to identify the relationship between strain point and fictive temperature reset, with the goal of an as-drawn sheet producing <10 ppm compaction after 5 min exposure at a temperature of 600°C—eventually this was increased to 675°C. Exploratory research in this topic had produced a number of interesting starting points for further development, and in 2007, the first development trials were attempted with these glasses. An early discovery was that due to some combination of overall composition, the specific melting process used, and the high temperatures required for fining the glass, antimony oxide appeared to be required to obtain the very high-quality glass required for p-Si applications. In addition to defects, p-Si devices often have much more stringent requirements for sheet shape, warp, etc., and thus much of the early effort was focused on the forming activities. A further complication was that the various thermal process steps used by Corning's customers were not only different from one to the next, but they were understandably loath to share them because of their proprietary nature.

It took several development trials in production tanks and several trial glass compositions before the right balance was obtained: a strain point of 741°, a whopping 75° higher than Eagle XG™, and one of the

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highest strain points for any commercially available melted glass of any kind. The remaining physical properties were very similar to conventional AMLCD substrates, save that the density was slightly higher than the normal industry standard. These attributes come with a cost: the melting and forming temperatures were the highest for any glass that Corning has manufactured in a continuous process. The final substrate product, named Jade™, was introduced in early 2008, and is currently gaining acceptance as a premium substrate for p-Si applications.

What Does the Future Hold?

It is a truism that the only certain way to fail is to make predictions, but with this firmly in mind we will hazard a few. We are reminded from time to time that Corning Display Technologies does not sell a glass, but a fusion-drawn surface. The glass is simply a support structure for that surface, and anything that can be performed to make it as unobtrusive as possible is a benefit to our customers. The fusion process has been adopted by several of Corning's competitors, and it is possible that others will follow in the coming years. It is a fact that we could not manufacture the sheet we make today using fusion-draw technology familiar to Dockerty, and it is all but certain that the fusion process will continue to evolve and improve. A key industry trend for many years has been larger sheets, which permit larger numbers of large panels to be made from each sheet of glass. The largest sheet currently used in AMLCD fabrication processes is Gen 10, 2850 mm × 3050 mm and—rather astonishingly—700 μm thick. Simply removing a sheet of these dimensions from a fusion draw becomes a daunting engineering challenge, much less packing it for shipping to the customer's fabrication plant. Simply supporting the weight of the isopipe and ancillary fusion-draw equipment becomes a nontrivial engineering problem at such sizes. It is an exciting time to be working on such an adaptable forming process.

The CTE and densities desired for future substrates are quite likely to be like those of today's substrate glasses, and thus there are many compelling reasons to stick with alkaline earth borosilicate and aluminosilicate glasses. As customers look to reduce the weight for mobile devices, inputting thinner substrates or etching the glass after TFT fabrication becomes an increasingly attractive option compared with seeking still lower densities for the substrates themselves. Larger sheet sizes and the need for a constantly improved throughput will likely keep a-Si processing temperatures in the same range as currently used, but the integrated impact of fictive temperature reset will be increasingly large as overall sheet size increases. One can envision a future in which a higher strain point glass will be required to meet these more demanding requirements. The same may well be true for p-Si substrates: higher strain points will result in an improved performance in customer processes, and as with 1737 and Eagle^{2000}, the desire to reduce or eliminate arsenic and antimony from such products is unlikely to go away.

Two new, interesting trends deserve some attention. Flexible displays and other flexible flat panel electronic devices have generated much attention recently (Chang and colleagues[60,61] and related articles in the same issue). By and large, the flexible display approach focuses on plastic because it is thin and flexible, and also because it can be used in roll-to-roll fabrication processes. It is interesting to consider what advantage glass might offer in such an application, provided that it could be made thin enough and tough enough. Much of the focus of flexible displays is aimed toward OLED-based devices, but these currently require p-Si TFT arrays to work, and must be hermetically sealed from any interactions with water and oxygen to ensure a continued operation for sustained periods of time. As noted above, thin, high strain point glass definitely enables low-temperature p-Si processing, and glass is intrinsically hermetic compared with nearly any plastic. Whether brittleness and high modulus (hence large bend radius) can be overcome remains to be seen, but it is an exciting possibility nonetheless.

The second interesting industry trend is toward touch-oriented devices, particularly touch-screen displays. Here, the appeal of glass is not just practical but esthetic; glass can be chemically or thermally strengthened against scratches and damage introduce by dropping in ways that are impossible with plastic, and has a cool touch that is often favored in the design of touch-based electronics. Corning already sells Gorilla™ Glass, a fusion-drawn sheet glass that can be ion-exchanged to produce an exceptionally tough compressive layer at its surface, thus resisting damage in the real-world use of mobile consumer electronics. It is possible that display panel makers will want to move away from a separate cover glass and use the CF glass itself as part of the touch-panel component of such a display. Were this to happen, then the CF glass might have to be engineered for enhanced toughness, and if industry trends toward thinner glass hold true, then thermal or ion

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exchange may not be enough to get there; the glass itself may have to have an intrinsic toughness well. This presents an exciting avenue for future composition research.

Conclusion

We have presented a brief history of substrate glasses developed by Corning for use in AMLCD displays. It should be obvious that no one at Corning sat down and came up with all the interlinking technologies represented by today's substrate glasses. Rather, interesting inventions in forming processes intended for entirely different applications (slot draw and fusion) were linked with compositions developed for entirely different applications (Codes 0211 and 7059) to give birth to a business, and the meteoric growth of that business spurred a wealth of process and material innovation. The evolution in the forming processes away from float or slot-draw to fusion is a response to the need for nearly perfect surfaces in TFT processing. The evolution in glass composition is to provide a surface that is nearly as possible insensitive to the thermal processing steps used in TFT fabrication. Current trends are toward thinner sheet, and enhanced thermal stability for the substrate glass itself, and possibly modifications of the base compositions to produce enhanced compositions for particularly demanding applications, such as flexible displays and touch-screen cover glasses.

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Appendix A: Terms Used in This Paper

Annealing point (T_{ann}): A viscosity corresponding to about $10^{12.2}$ Pa s, and therefore roughly equal to the more traditional glass transition temperature (T_g), rather arbitrarily defined as the temperature corresponding to 10^{12} Pa s. T_{ann} is measured by fiber elongation[62] and beam bending viscometry.[63] Typical values for display substrates range between about 630°C and 800°C.

Fining (also called refining): a process wherein chemical changes, increased temperature, or imposition of vacuum is used to remove bubbles from a glass melt. Chemical fining is accomplished by releasing gas into existing bubbles at high temperature, for example, reducing multivalents dissolved in the glass to release oxygen into bubbles. Thermal (or Stokes) fining is accomplished by increasing the temperature of a glass melt; this causes existing bubbles to expand and decreases viscosity, thus accelerating the rate of bubble rise. Vacuum fining is accomplished by forcing glass up a vertical column, thus causing a decreasing head of pressure and encouraging bubbles to expand. In practice, two or more of these procedures are used to produce bubble-free glass.

Linear coefficient of thermal expansion (usually abbreviated CTE): the ratio of the difference in length of a rod or bar of glass measured at two temperatures (generally between room temperature and 300°C) and the difference between the two temperatures, typically measured via push-rod dilatometry.[64] Typical units for glasses are ppm/°C or 10^{-7}/°C. Typical ranges for display glasses are between 31 and 48×10^{-7}/°C. Changes in the dimensions of a glass object with changes in temperature that arise entirely from CTE are reversible, and when the original reference temperature is restored, the object will recover its original dimensions.

Liquidus temperature (T_{liq}): The maximum temperature at which a crystal is in equilibrium with a glass melt. It is a difficult measurement to perform, thus a more typical definition is operation, for example, the highest temperature at which a crystal is seen after 24 h in a gradient boat furnace.[65]

Fictive temperature (T_f): A widely used but rather poorly defined term describing the disparity between the structural characteristic of a glass at a particular temperature compared with the structural characteristics that would be obtained if the glasses were thoroughly equilibrated at this temperature. Various descriptions of fictive temperature are discussed by Mauro *et al.*[66] For the purposes of our discussion, we will use temperatures or viscosities to describe the disparity between the configurational states in a glass versus those that would be obtained if the structure equilibrated at the temperature of interest, and likewise to compare different structural

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states imposed by different processes. A glass that is cooled rapidly from high temperature has a higher fictive temperature than a glass that is cooled slowly from high temperature.

Compaction: An irreversible decrease in the dimensions of a glass object caused by reheating the object to a temperature close to its fictive temperature, such as in the thermal processing of a-Si to develop a material suitable for thin-film transitor arrays. For a given process temperature, higher fictive temperature results in greater compaction. For a fixed fictive temperature, higher process temperature results in greater compaction.

Strain point (T_{str}): A viscosity corresponding to about $10^{13.2}$ Pa s, measured by fiber elongation[66] and beam bending viscometry.[66] Typical values for display substrates range between about 550°C and 750°C.

Density: The mass of dense glass per unit volume (e.g., grams/cc) and typically measured via the displacement of water by a powder or solid sample in a pycnometer.[64] Most display glasses fall between about 2.38 and 2.78 g/cm^3.

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