PRODUCTION and PROPERTIES of ULE® GLASS with REGARDS to EUV MASKS

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The processing and properties of Corning Incorporated's ultra-low expansion (ULE®glass) glasses for use in EUV (extreme ultraviolet) masks is reviewed. The properties reviewed include ULE®glass's coefficient of thermal expansion (CTE), low temperature thermal cycling information (T<300°C), high temperature (T>1300°C) crystallization behavior, some polishing results and Corning's CTE measurements. A second section of this paper identifies some of the steps being taken at Corning Incorporated to further characterize the material for specific use as EUV masks.

INTRODUCTION

ULE®glass is being considered for application as the substrates for EUV masks, primarily because of its *ultra*-low coefficient of thermal expansion (CTE). A low CTE identifies the materials stability against temperature changes. However, there are many more material property requirements that are needed for EUV substrates. These will be discussed. An excellent detailed review of ULE®properties was provided by Gulati and Edwards [1].

The objective of Corning Incorporated at this time is to present ULE®glass material property data that already exists which is pertinent to applications in EUV applications. A second objective is to identify the steps being taken at Corning Incorporated to further characterize our material for specific use as EUV masks. It is expected that the requirements will evolve as the industry begins to evaluate the substrates within actual equipment runs. To date, only limited tests have been carried out on actual low expansion substrate material, because the EUV community has been working out the issues of equipment manufacture and performance while using tried and true silicon wafers. The switch from silicon wafers to actual low expansion substrate materials is going to take place soon.

HISTORY and DEFINITION

Corning Incorporated has been making ultra-low expansion (ULE) glass since the 1960's. The glass's primary application has been for use in telescope mirrors, both orbiting telescopes and terrestrial bound telescopes; examples of which are shown in **Figure 1**. The well known Hubble space telescope is shown in Figure 1a and a larger 8.1 m diameter Gemini telescope mirror blank is shown in Figure 1b. Both were manufactured with Corning Incorporated's ULE®glass. These large mirrors require low expansion material to minimize

distortions in the images resulting from thermal changes. This same low expansion property is one of many properties that makes it a prime candidate for use in EUV masks.

ULE®glass, as stated above, stands for Ultra Low Expansion glass (ULE) and is defined as having a coefficient of thermal expansion (CTE) of 0±30 ppb/°C over the temperature range of 5 to 35°C **(Figure 2)**. To provide perspective, this is more than an order of magnitude smaller than the coefficient of thermal expansion of fused silica, which is traditionally considered to have a small expansion, with a CTE of about 500 ppb/°C (0.5×10^{-6}/°C) over the same temperature range [2].

ULE®glass is sold in different grades with the premium grade having the lowest CTE range of only 10 ppb/°C. The requirements for the EUV community have not yet been rigorously defined, so that it is unknown which grades of glass would be required for different EUV applications. Mirror grade glass, for example, has a CTE range of 15 ppb/C or less.

A CTE range of 10 ppb/°C means that the ultrasonic CTE measurements anywhere within the glass will not vary by more than 10 ppb/°C. To illustrate this, all of the following glasses are considered premium grade ULE®glass: (1) ULE glass with a CTE between -5 ppb/°C and +5 ppb/°C. (2) ULE®glass with a CTE between +20 ppb/°C and +30 ppb/°C (3) ULE®glass with a CTE between –20 ppb/°C and -30 ppb./°C. (4) ULE®glass with a CTE between 0 and 5 ppb/°C. Note that the CTE never exceeds +30ppb/°C and never goes below –30 ppb/°C and the total range is less than 10 ppb/°C within a given specimen.

The CTE in ULE®glass is a function of the titania concentration. As the titania concentration increases, the CTE decreases **(Figure 2)**. The composition of the glass is tailored to meet the CTE specification.

ULE®glass is unique from other low expansion materials in that it is a glass and not a glass-ceramic. Example of low expansion glass ceramics are Zerodur® as well as Corning Incorporated's low expansion glass-ceramic: code 9600. (Code 9600 glass- ceramic has been discontinued). There are no crystalline phases present within ULE®glass. In other words, ULE®glass is completely amorphous as illustrated by the TEM image of ULE®glass shown in **Figure 3a**. This makes it unique from other low expansion materials such as Zerodur® and Corning Incorporated's code 9600 glass-ceramic. A TEM image **(Figure 3b)** shows the crystals present in Corning Incorporated's code 9600 low expansion glass-ceramic. The crystals within these particular glass- ceramics have a negative coefficient of thermal expansion and are embedded within a glass matrix with a positive coefficient of thermal expansion.

PROCESSING

ULE®glass is also unique from other glasses in the method in which it is formed. Conventional glass is fabricated by mixing raw material powders together into a batch. The melted batch is then poured. However, ULE®glass is a high temperature glass which makes it unsuitable for manufacturing by conventional means. Instead of being poured, it is fabricated by a flame hydrolysis process **(Figure 4)** which is similar in scope to chemical vapor deposition. Here, high purity precursors are injected into flames which then react to form TiO_2 and SiO_2 which deposit onto the surface of the growing glass. The process has the advantage of minimizing impurities. Impurities such as sodium and other alkali/alkaline earths are typically on the order of a couple ppm or less. This high purity should be attractive to the semiconductor industry.

PROPERTIES

STABILITY AGAINST CRYSTALLIZATION

The crystallization behavior of ULE®glass at temperatures over 1300°C was reported by Mazurin et al.[3]. This paper focused on crystallization on a cleaned ULE®glass and high purity fused silica [HPFS®] glass surfaces in air. For these conditions, the induction period for crystal nucleation increased as the temperature decreased. The data from Mazurin et al. was obtained at high temperatures where reasonable nucleation times could be measured, and it suggested that no nucleation in reasonable times (days) at temperatures below about 1100°C should occur on a cleaned surface.

The data of Mazurin et al. also showed the growth rate in ULE®glass at these same temperatures (1300-1400ºC) once nucleation had occurred. The data shown in **Figure 5** was taken from Mazurin et al.'s paper. The lowest growth rate reported was under 10 µm/hr at 1300°C. The data suggested growth rates of less than 1 Å/hr at 800°C for these pristine surfaces. These are obviously outrageous extrapolations, but they simply illustrate that pristine ULE®glass is not expected to undergo devitrification at low temperatures.

No data was found on crystallization of contaminated ULE®glass. However, a similar glass with appreciable data is vitreous silica. Mazurin et al. [3] showed that for the same crystal growth rates and nucleation times, ULE®glass was about 100°C to 125°C lower in temperature than vitreous silica. The fused silica literature indicates [4] that vitreous silica can be used continuously at temperatures of 1000°C or less without crystallization occurring:

> *Transparent silica can normally be used in air continuously at temperatures up to 1000°C and for short periods up to 1250°C without devitrification occurring. This recommendation assumes, however, that the glass surface is substantially free of alkali contamination which can occur from sources, such as airborne dust or fingerprints [4].*

Therefore, this would suggest that ULE®glass could be used continuously at temperatures of 800°C and less under the same conditions.

STABILITY AGAINST THERMAL CYCLING

The data available in the literature indicates ULE®glass is dimensionally stable after thermal cycling (See Table 1). Shaffer and Bennett [5] report changes to the figure of ULE®glass while heating to 350°C, but no residual or permanent figure change after cooling again to room temperature, even after extreme cooling by water quenching. Jacobs et al. [6] monitored surface figure changes while thermal cycling specimens from room temperature to 200°C and back to room temperature. The instrument repeatability was reported to be about 13 nm and a measured change within ULE®glass was less than 13 nm for non-uniform heating of the glass. Also, no thermal expansion hysteresis was observed within ULE®glass during this study. Therefore, it was stated that no appreciable figure change took place during thermal cycling at temperatures below 200°C. These results show that ULE®glass looks very promising for use in EUV applications where stability is required.

STABILITY AGAINST MECHANICAL CYCLING

This type of stability refers to permanent changes taking place in the substance as it is mechanically loaded and unloaded. It has importance in cases where clamping stresses are applied during grinding and or polishing. Once the stresses are removed, it is desirable to have the sample spring back instantaneously without having a time dependent response referred to as a "delayed elastic response." Pepi and Golini [7] reported that no delayed elastic response was observed in ULE®glass (detection limit of 10 nm rms). They expected none in this glass based on its low sodium content. It appeared to be stable against mechanical cycling.

Elastic hysteresis within ULE®glass was examined by Wilkens et al. [8] at 300°C and 600°C. This refers to mechanically cycling the glass at these different temperatures. Elastic hysteresis indicates that some permanent change takes place and this was observed in ULE®glass at 600°C, but not at 300°C. This suggested that some amount of creep within the glass took place at 600ºC. It also suggested no measurable amount of creep for use at temperatures of 300°C and less.

POLISHING of ULE GLASS

No known insurmountable polishing issues exist that would prevent ULE®glass from being polished to the finish required at this time by the EUV community. Shown in **Figure 6** is an atomic force micrograph of ULE®glass that has been polished to 1-2 Å rms surface roughness at Corning Incorporated [9]. In a separate paper, Tong et al. [10] have demonstrated that ULE®glass can be polished to 0.5 Å rms surface roughness.

CTE MEASURMENTS AT CORNING INCORPORATED

Corning Incorporated's ability to measure the coefficient of thermal expansion within ULE®glass is one of the best in the world. Some of the important characteristics of the technique are summarized in Table 2. This valuable diagnostic tool has an accuracy of ±2ppb/°C with even better precision [11,12]. It has been in use in a production facility since 1973 and thus is reliable. Additionally, the measurements are non-destructive, such that the CTE can be measured in actual parts. This makes the measurement a powerful diagnostic tool. Many alternative CTE measurements require samples to be cut to specific dimensions. This means that there CTE measurements are from areas surrounding the parts, but not from the actual part. Finally, our CTE measurements can be measured at spacings of about 1 cm. This also makes the measurements valuable for mapping out CTE within actual parts with no required guess work.

The actual property measured is the ultrasonic velocity within the glass. This velocity has been correlated to the CTE for ULE®glass [11]. Figure 7 shows how the ultrasonic velocity is measured. A pulse is sent through the glass of known thickness, and the time to travel through the glass is measured [2]. The distance over the time is the ultrasonic velocity. This velocity is dependent on a number of material properties as shown by the equation in **Figure 7**; the density, Poisson's ratio and elastic modulus of the glass. The elastic modulus increases as the amount of titania increases, but density and the Poisson's ratio remaining about the same. The CTE is also strongly dependent on the titania concentration such that ultrasonic velocity is correlated to the CTE. The correlation study by Hagy and Shirkey revealed an

accuracy of ±2 ppb/°C. In a later paper, Edward's et al. [12] showed an even better precision by this method, making it one of, if not the best CTE measurement capability available for ULE®glass.

UPCOMING EFFORTS

Corning Incorporated has strong capabilities in the area of CTE measurements, birefringence measurements and also modeling. These capabilities are being combined to develop a powerful set of diagnostic tools. The goal is to use the CTE measurements to predict the birefringence values within the glass and then to compare actual birefringence values to predicted values as illustrated in **Figures 8 and 9**. This will help identify the source of birefringence throughout the glass.

The CTE measurements at Corning Incorporated allow the CTE to be measured in the actual parts at 1 cm spacings to an accuracy of ±2 ppb/°C. The birefringence measurement capabilities allow birefringence to be measured to a similarly high level of accuracy of less than 1.0 nm/cm with capabilities of mapping birefringence at a spacings of about 1 mm. Both measurements will be employed. Finally, a model has been previously developed to predict the birefringence within samples based on the CTE distribution within the glass. This model has proven to be accurate within large 1.5 m diameter boules but it has yet to be tested on small 15 x 15 cm samples. This will be the next step. This set of tools (CTE measurements, birefringence measurements and model predictions) results in a powerful set of diagnostic tools which will allow Corning Incorporated to respond and adapt quickly to customer requirements.

CONCLUSIONS

Corning Incorporated currently produces ULE®glass which appears promising for use as EUV substrates based on its low coefficient of thermal expansion. Many other material properties which have been reported in the literature also indicate that this material will be an excellent choice for EUV substrates. These properties include its stability against crystallization, stability against thermal cycling, stability against mechanical cycling as well as its polishing behavior. Corning Incorporated has the further advantage of being capable of characterizing the CTE within parts to a high accuracy and ability to measure the CTE non-destructively on actual parts and to map the CTE within those parts at 1 cm spacings. Combining this with birefringence measurements and model predictions results in a powerful set of diagnostic tools for EUV developers.

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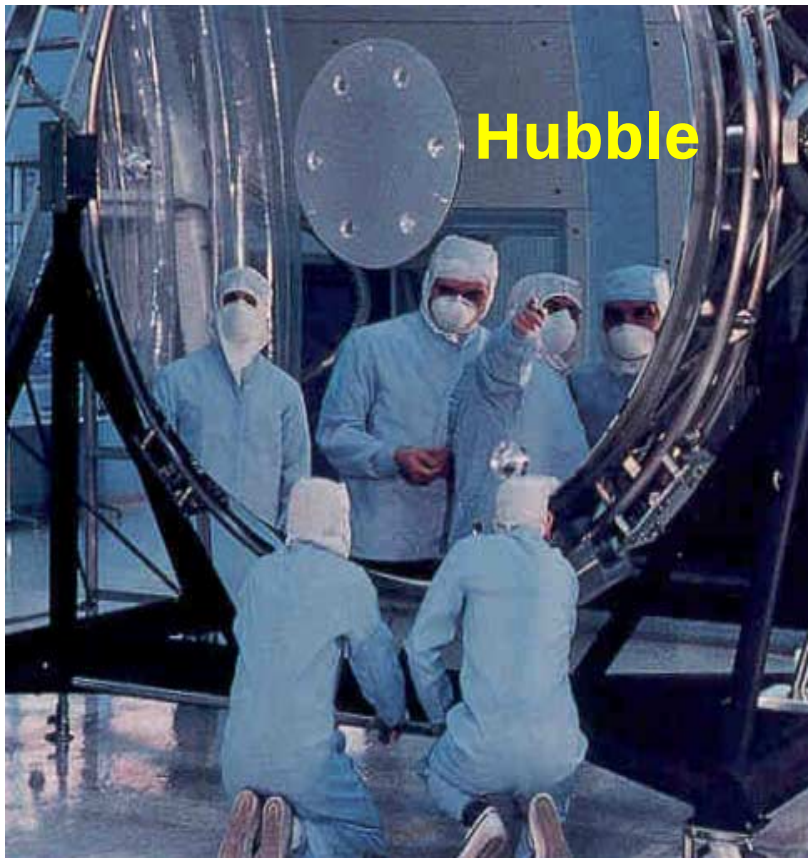


Figure 1. Corning has a long history of making ULE® glass since 1960's. On the left (a) is the mirror used in the Hubble space telescope and on the right (b) is the 8.1 m Gemini mirror now in Hawaii, both are made with ULE® glass.

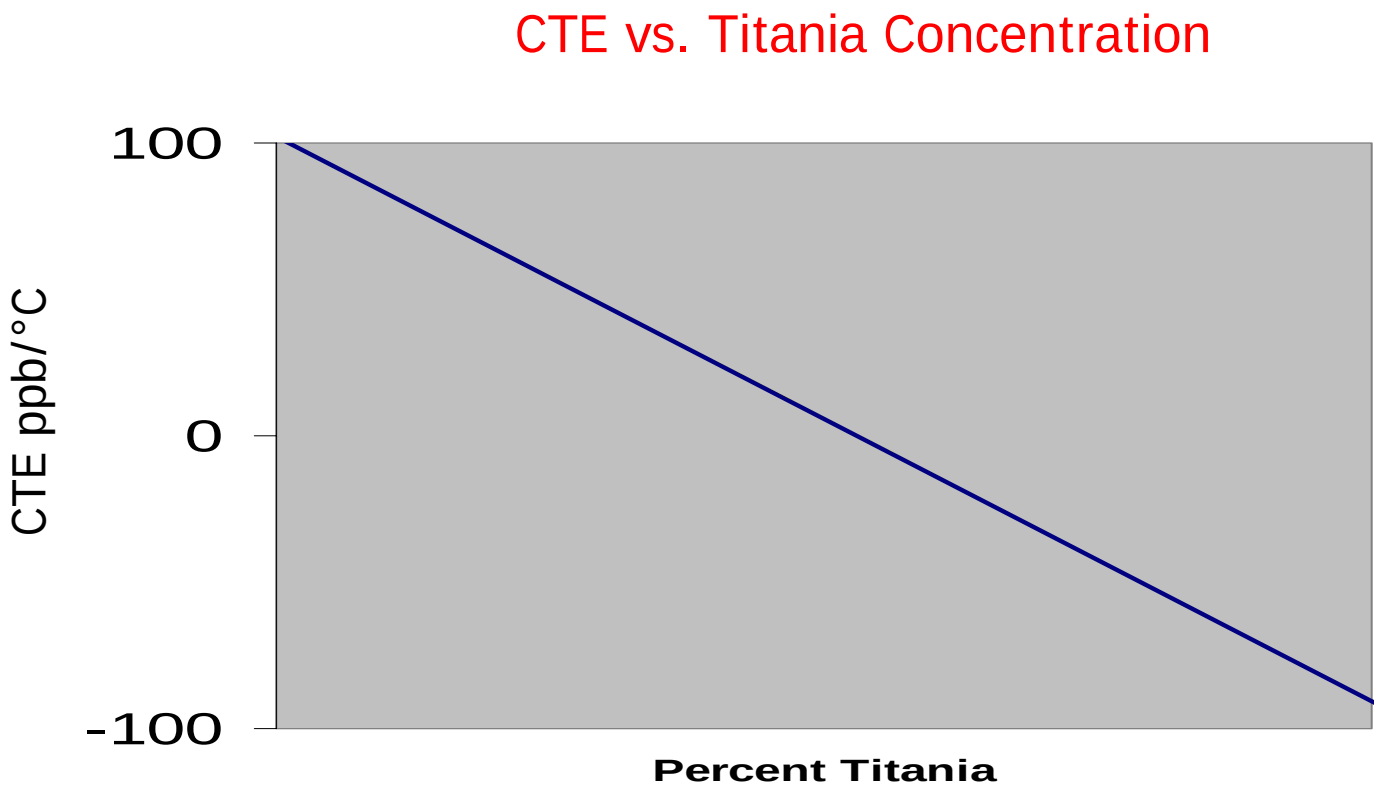
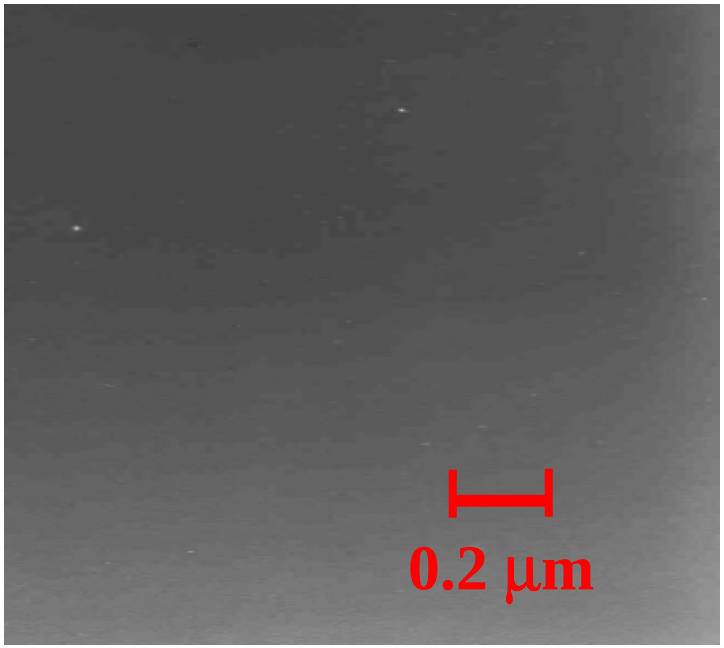


Figure 2. ULE®glass (ultra-low expansion) is defined as having a coefficient of thermal expansion (CTE) of 0±30 ppb/°C over the temperature range of 5to 35°C. ULE® glass is a binary glass with approximately 7 weight percent titania. The plot simply demonstrates that the CTE decreases as the titania level increases. ULE ® glass is divided into different grades with the premium grade glass having the smallest CTE range of 10 ppb/°C or less within the glass.

TEM micrographs

ULE® Glass



Corning's low expansion 9600 glass ceramic

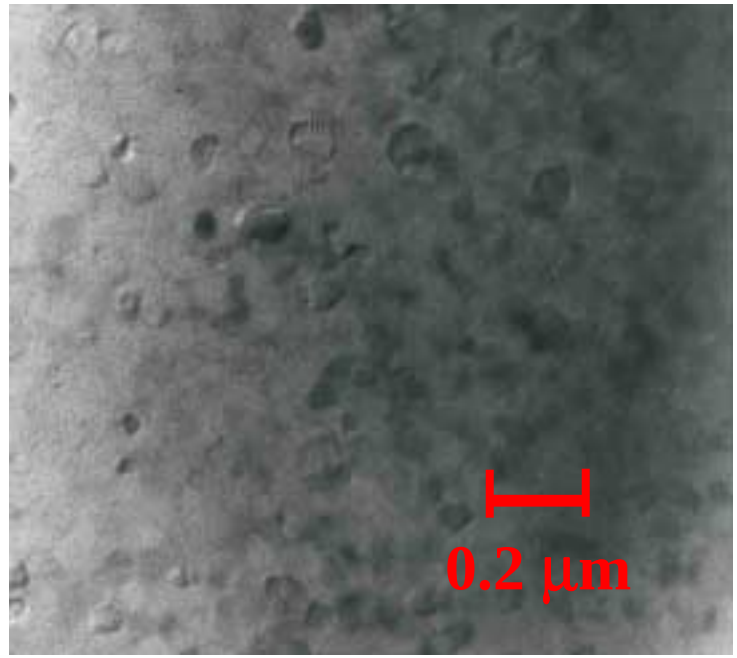


Figure 3. TEM micrographs of: (a) (left) ULE®glass (ultra-low expansion) is single phase and completely amorphous with no crystals present. (b) (right) A low expansion glass ceramic (Corning code 9600, now discontinued). Glass ceramics contain an amorphous glassy phase with positive thermal expansion and a crystalline phase with negative thermal expansion. The overall expansion is near 0 ppb/°C for both materials.

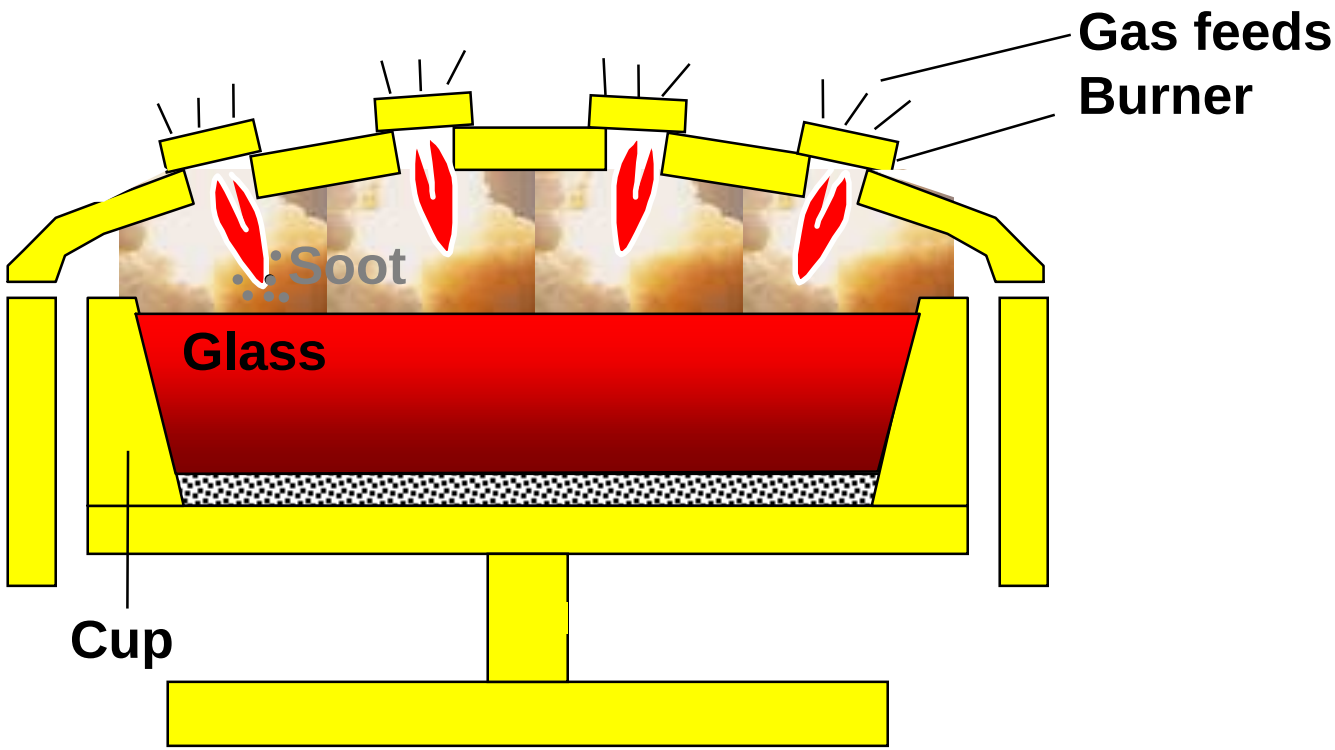


Figure 4. ULE®glass (ultra-low expansion) is unique from other glasses in how it is produced. The glass precursors are injected into a flame where they react and deposit, eventually forming bulk materials.

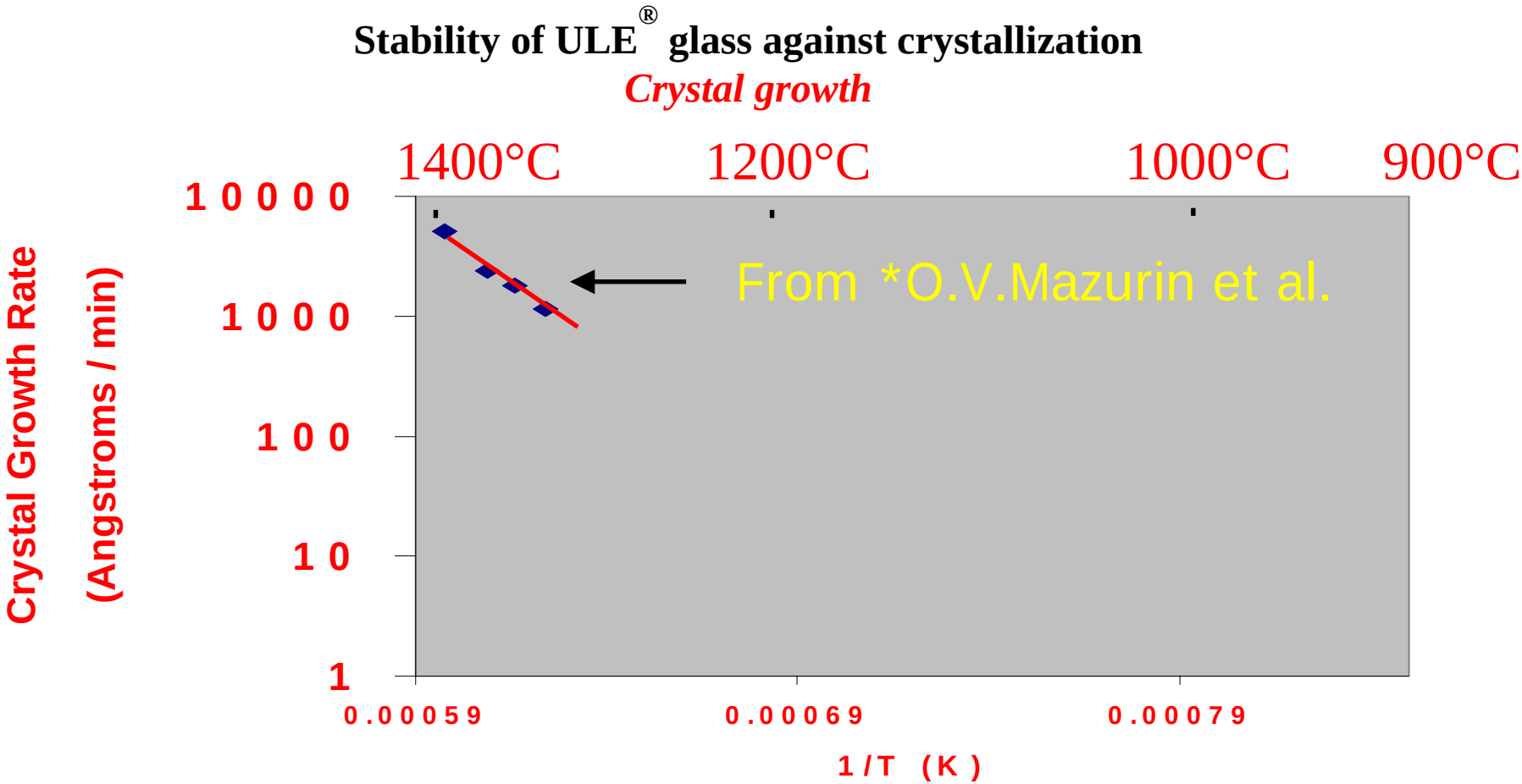


Figure 5. ULE®glass (ultra-low expansion) is a high temperature glass which is stable against crystallization. This graph contains data taken from Mazurin et al. [3] showing small growth rates. No data was found for the lower temperatures where crystal growth rates are expected to be small.

Stability of ULE® glass

Thermal Stability	***Mechanical Stability***
• "No change in optical figure is observed after quenching." 350°C quench [5] • "no significant hysteresis figure distortion…" under conditions of study [6]: – temperature cycles: • 25°C to 200°C – ~Distortion below instrument repeatability of 13 nm rms	• No measurable delayed elastic effect in ULE at room temperature [7] – detection limit 10 nm rms – None expected with low alkali material • Elastic hysteresis observed during loading/unloading at 600°C but not at 300°C [8]

Table 1. ULE®glass (ultra-low expansion) is stable. This table simply summarizes some of the reports on: (a) thermal stability and (b) mechanical stability.

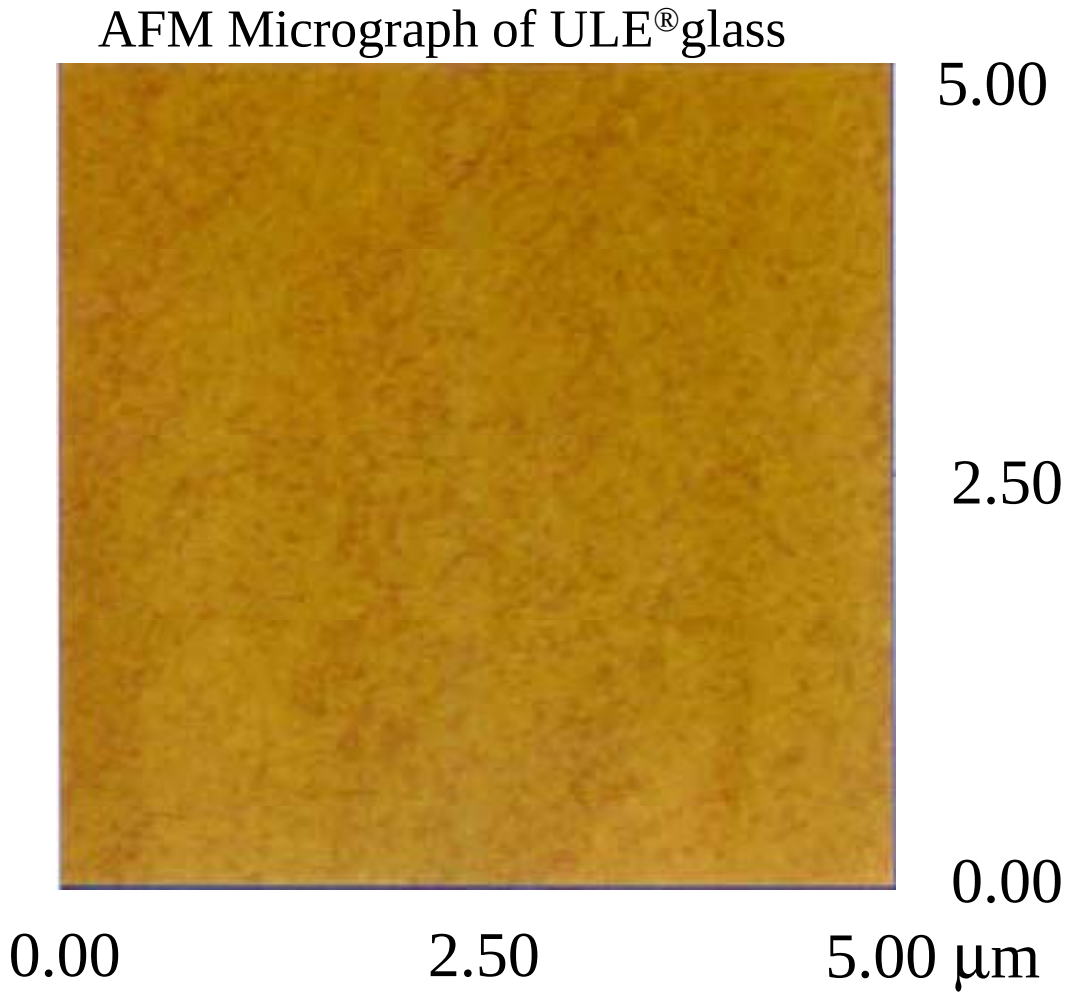


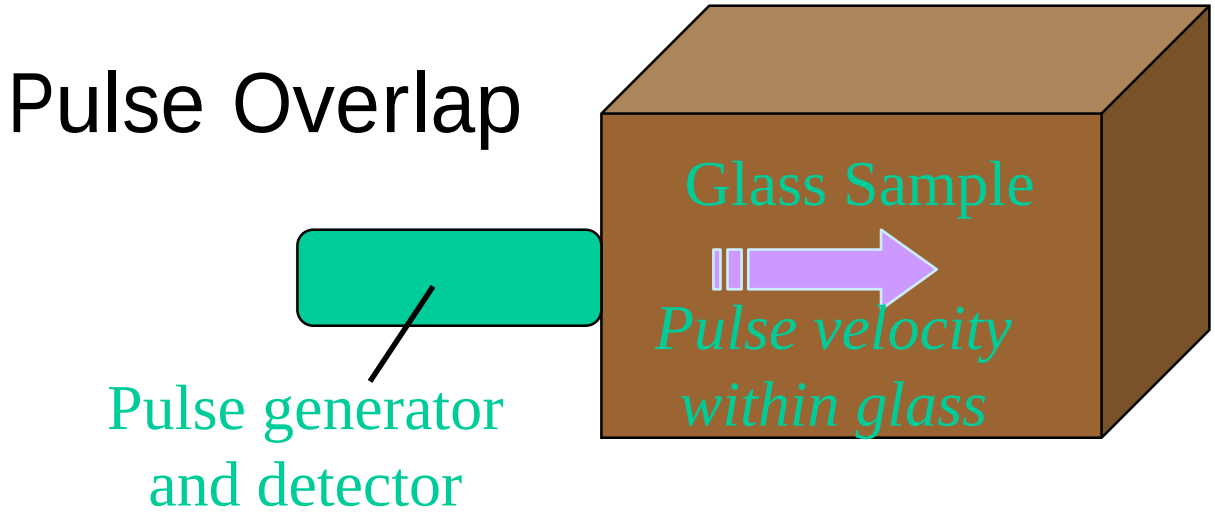
Figure 6. ULE®glass (ultra-low expansion) has been polished at Corning Incorporated to 1-2 Å rms in 1999 [9]. Others have reported values of 0.5 Å rms [10]. No known polishing issues exist which would prevent ULE ® glass from being polished to the values required for EUV substrates.

CTE Measurements at Corning Incorporated

- Accurate… absolute CTE measured to ±2 ppb/°C [11]
- Relative measurements better than ±2 ppb/°C [12]
- Reliable (in use since 1973)
- Non-destructive
- Measurements made with better than 1 cm resolution

Table 2. Corning Incorporated's ultrasonic CTE measurements are among the best in the world with many important characteristics, such as those listed here.

Measured Ultrasonic velocities correlated to CTE [11]



Velocity, V, related to properties of glass [2]:

$$V = k \left[\frac{E(1-\mu)}{\Downarrow(1+\mu)(1-2\mu)} \right]^{1/2}$$

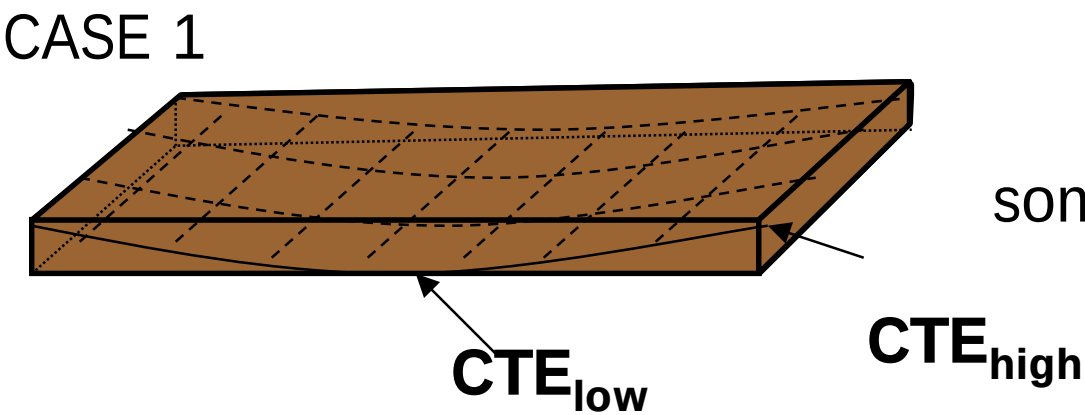
k = constant
E = elastic modulus
μ = Poisson's ratio
$\Downarrow$ = density

Figure 7. This schematic illustrates how the CTE is determined in ULE®glass. Both CTE and ultrasonic velocities change as the titania concentration changes within ULE®glass. Hagy and Shirkey [11] correlated the CTE to the ultrasonic velocities. The pulse overlap measurement technique was used. The above equation shows how the velocity is related to the properties of the material [2].

Birefringence in ULE® glass

Figure 8. Birefringence in ULE®glass (ultra-low expansion) is measured on a regular basis in 1.5 m diameter boules. Additionally, models have been developed [11] which predict the birefringence within the boules based on the CTE distribution within the glass. The measured birefringence is found to correlate with the predictions from the model. One of the next steps Corning Incorporated is taking is to apply the model to EUV substrates.

Contribution to birefringence from CTE… preliminary model predictions



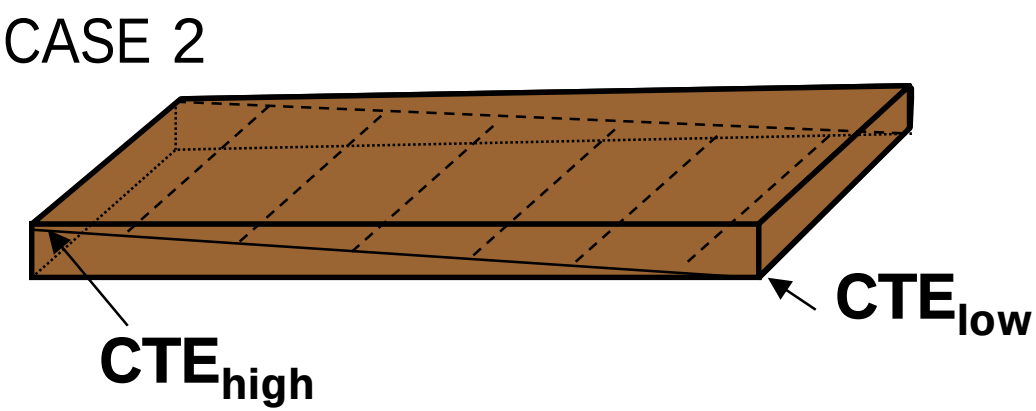


Figure 9. The preliminary model prediction of birefringence in ULE®glass (ultra-low expansion) based on CTE distribution alone is shown here [11]. Case 1 indicates birefringence would be present for a parabolic CTE variation within the glass. Case 2, the model predicts that no contribution to birefringence is present when a linear CTE variation occurs. A more detailed report is planned.