Glass Processing

Lecture #18. Silica Glass Processing Part 2

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Lectures available at:

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Day Two
Synthetic Fused Silica

Outline

Day One

1. Introduction - Silica Glass (SiO_2) - Its technological importance (Properties, Applications)
2. Innovations in manufacturing history
3. Type classifications for vitreous silica
4. Silica glass from natural raw materials

   Processes and resulting characteristics

Day Two

1. Synthetic fused silica manufacturing

   Processes and resulting characteristics

   Deliberate addition of modifying chemical species.

2. Modern Applications

   Examples -Telescope mirrors, microlithography optics, optical fiber

3. Summary and Acknowledgements

Transparent Fused Silica Types

Chart to Assist Memory

	Electric Melting	Flame Fusion	
Natural Quartz	Type I	Type II	Less Pure
Synthetic Precursors	Type IV	Type III	More Pure
	Dry	Wet	

Type III - Synthetic Fused Silica Vapor Phase Deposition

Flame Hydrolysis

- Similar to flame fusion, except a silicon compound vapor (gas) is fed into the flame.
- Chemical reaction generates a white soot.
- Essential elements
  - Vapor source
  - Burner (hydrogen or methane with oxygen)
  - Substrate
- Illustrations from original J.F. Hyde patent

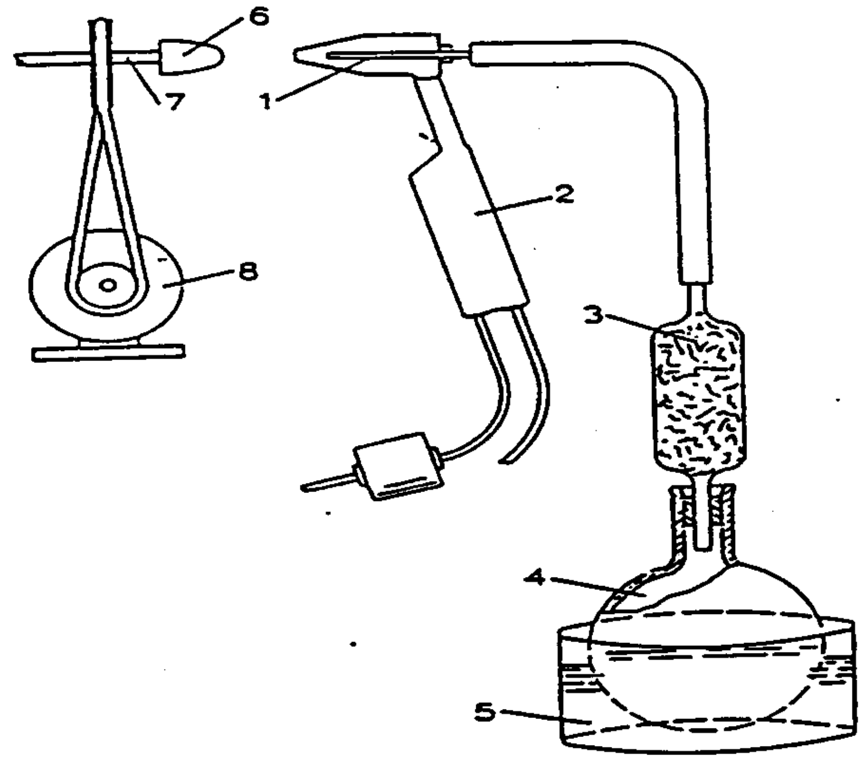


Figure 6. Flame Fusion of Synthetic Silica

1. Feed tube.
2. Oxy-hydrogen burner.
3. Filter tower.
4. Flask containing silicon compound.
5. Water bath.
6. Vitreous silica core.
7. Spindle.
8. Motor.

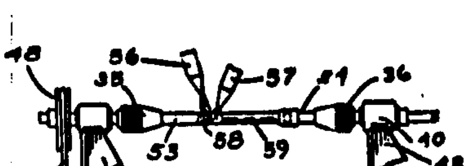


Fig.5

Synthetic Fused Silica Chemistry

- Flame Hydrolysis

  $SiCl_4 + 2H_2O \;=\; SiO_2\ (\text{soot}) + 4HCl\ (\text{gas})$

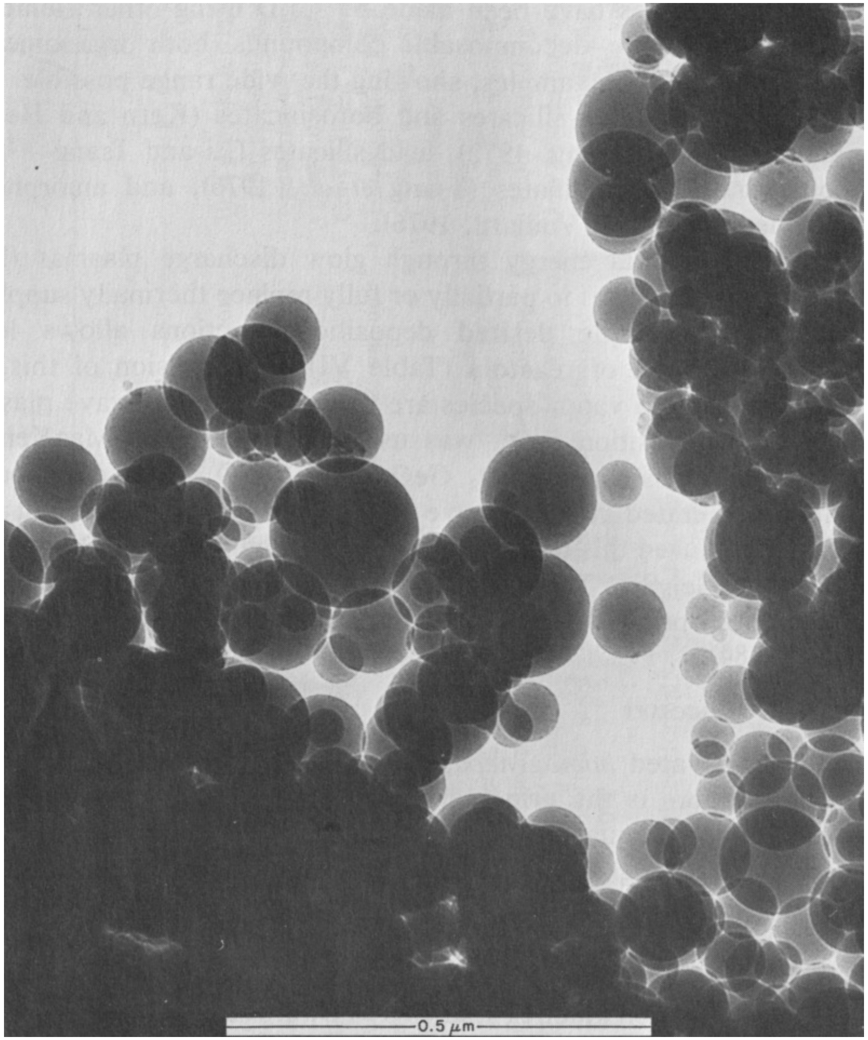
- Vapor Phase Oxidation

  $SiCl_4 + O_2 \;=\; SiO_2\ (\text{soot}) + 2Cl_2\ (\text{gas})$

  - Both are oxidation processes.
  - Hydrolysis dominates in hydrogen and hydrocarbon flame reactions.
  - HCl and Cl_2 are not environmentally friendly byproducts

Silica "Soot"

- Particle size about 100 nm with a total surface area greater than 20 m^2/gm.
- If substrate is maintained above about 1800 °C, simultaneous viscous sintering leads to a solid, bubble-free glass with a smooth surface.
- Substrate temperatures below about 1500 °C lead to porous, partially sintered bodies that can be fully sintered (consolidated) in a subsequent step.



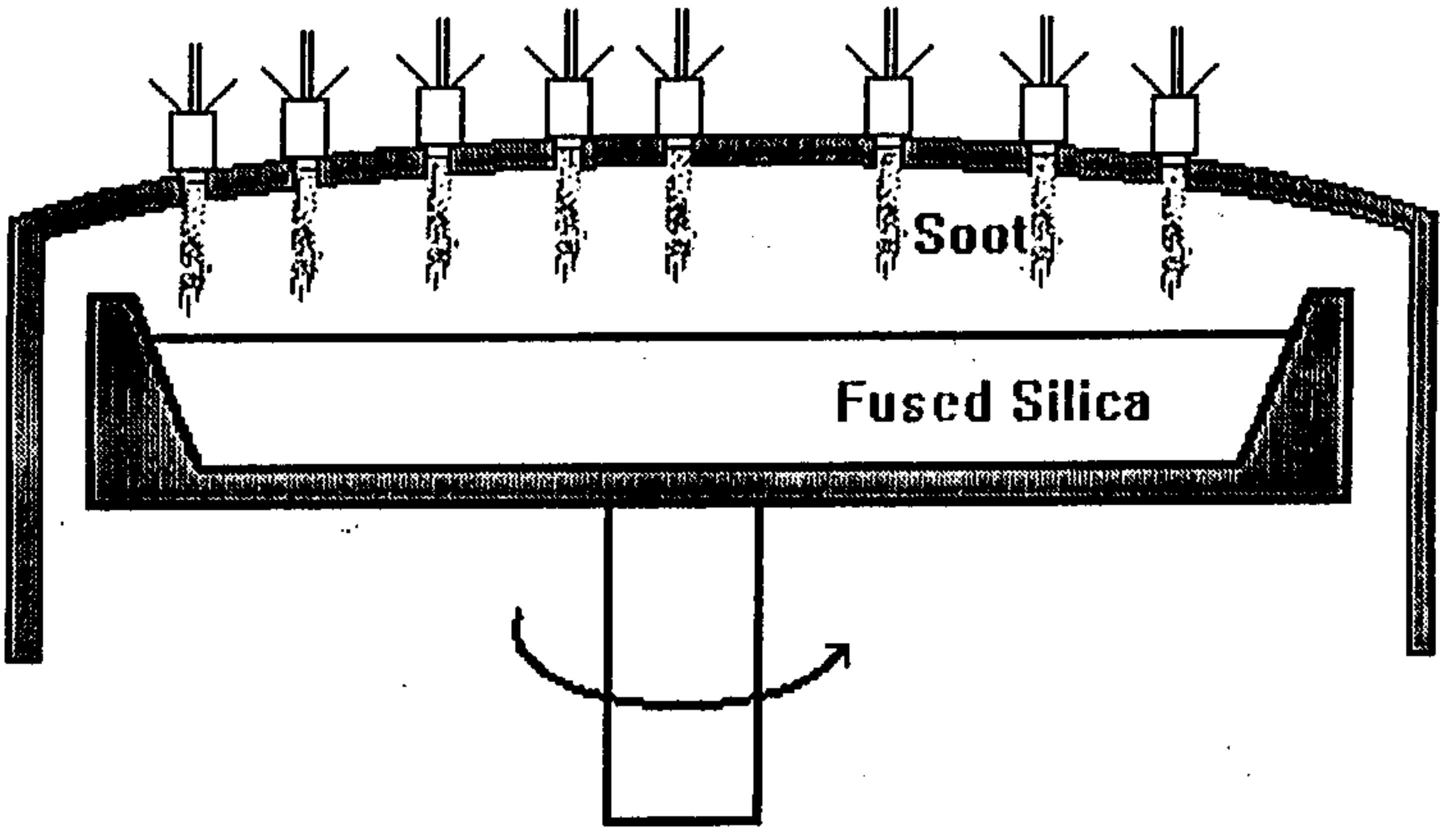
From Schultz and Scherer, 1983

Soot Deposition

- Deposition rates greater than 1.5 gram/minute were achievable from a single burner in the 1970s, considerably more now.

- Can be scaled up by using multiple burners

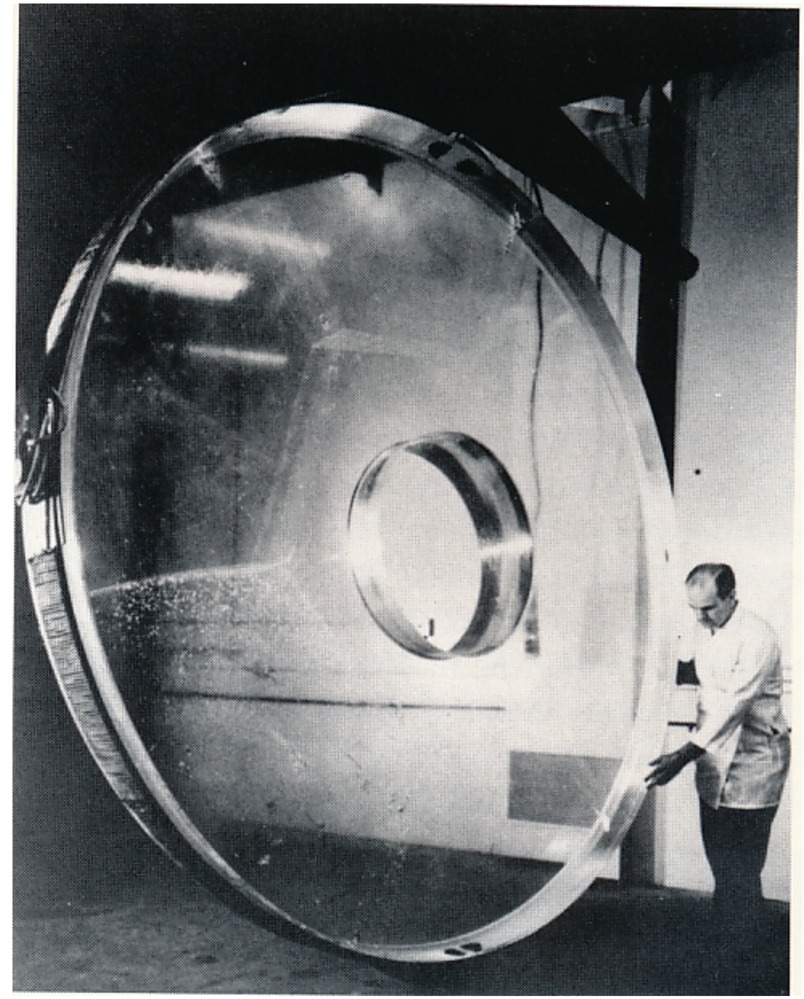
Corning 7940 and 7980 Process



Courtesy of Corning Incorporated

Fused Silica Telescope Mirror

- 108″–diameter fused silica mirror blank made for a University of Texas astronomical telescope.
- Made by fusing together hexagonal blocks, each cut from individual boules (Hex-seal process), then boring the central hole, grinding and polishing.
- Note the outlines of the hexagons.
- Note also that once the blank is ground and polished to its final "figure," it will be coated with reflective aluminum, so the hex lines are of no consequence.



Corning Incorporated Product Literature

Environmental Friendly Precursors

- Environmentally more-friendly precursors - chain and cyclic siloxanes
  - M.S. Dobbins and R.E. McLay (Corning)
    - U.S. Patent 5,043,002 (1991)
  - I.G. Sayce, A. Smithson and P.J. Wells (Thermal Syndicate Ltd. / St. Gobain)
    - British Patent 2,245,553 (1992)

Corning Code 7980 and Later Processes

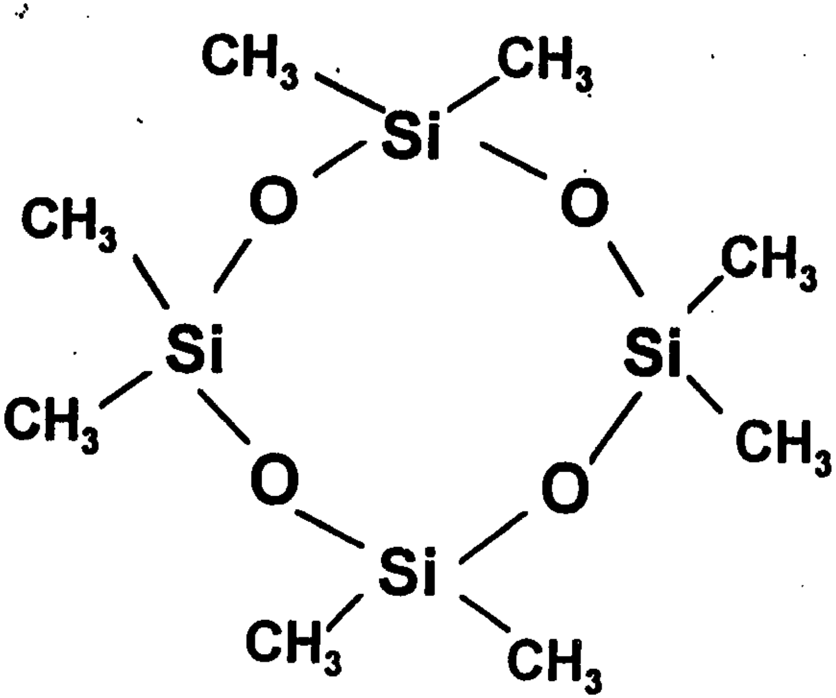
Replaces $SiCl_4$ by OMCTS

Combustion products

SiO_2
CO_2
H_2O

No Cl_2 or HCl

Environmentally friendly



OMCTS
Octamethylcyclotetrasiloxane

Heraeus Type III

- This is still a "boule" process, although the boules are considerably smaller than in Corning's 7980 process.

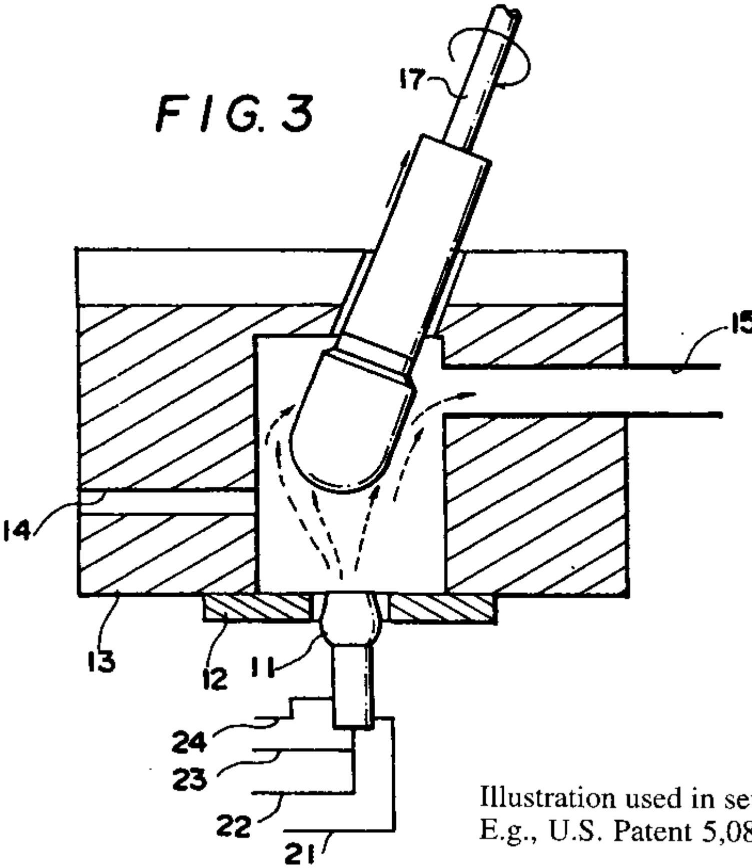
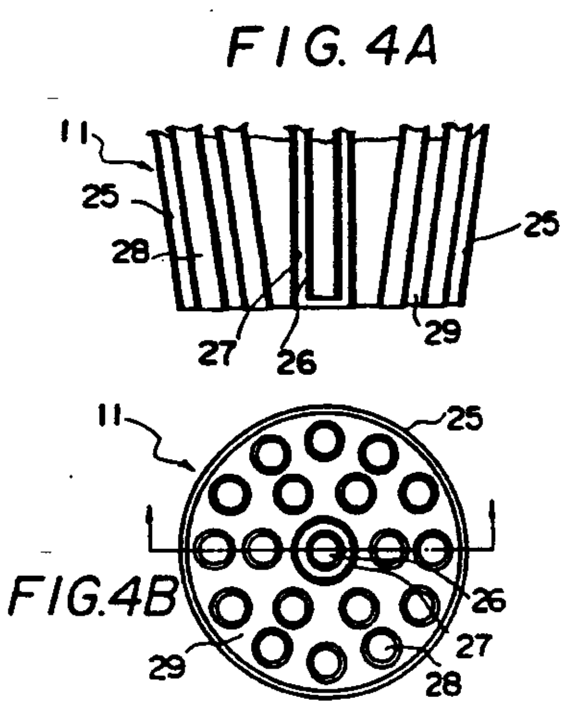
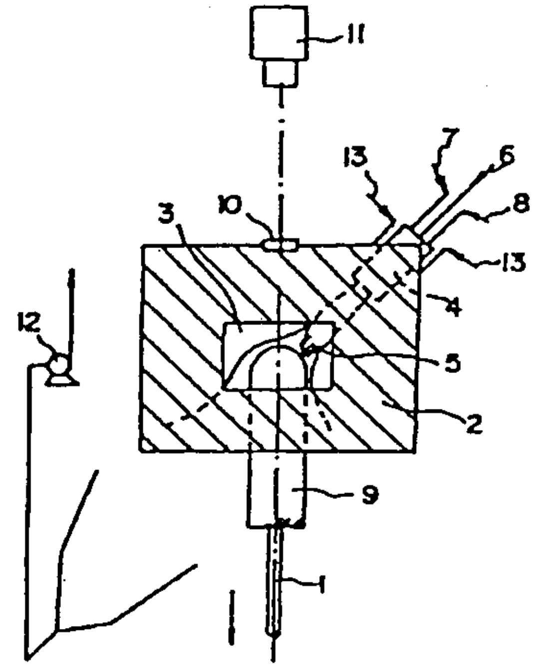


Illustration used in several Heraeus patents
E.g., U.S. Patent 5,086,352 (1992)

Heraeus - Shin Etsu Type III



Burner Face Design



1. Heat-resistant support
2. Adiabatic material
3. Reaction chamber
4. Oxygen-hydrogen burner
5. Oxygen-hydrogen flame
6. Silicon compound
7. Oxygen gas supplying entrance
8. Hydrogen gas supplying entrance
9. Synthetic quartz glass rod
10. Viewing window
11. Radiation temperature gauge
12. Exhaust gas blower
13. Oxygen gas supplying entrance

Summary - Silica Glass - Type III

- Synthetic - Hydrolysis of $SiCl_4$ or other precursors in oxy-hydrogen or oxy-natural gas flame
- Silica "soot" collected & sintered on boule
- Wet" - 600 to 1200 ppm OH
- Low metallic impurity < few ppm; some Cl (50 to 100 ppm) if $SiCl_4$ used
- Examples:
  - Suprasil (Heraeus)
  - Spectrasil (TSL)
  - Tetrasil (Quartz et Silice)
  - P-10 (Shin Etsu)
  - Corning 7940 and 7980
  - Dynasil 1000 (Dynasil)
  - Nippon Silica Glass – ES
  - G.E. Type 151 (General Electric)

Exercise

- Comparing the flame fusion process (Type II silica) and the flame hydrolysis process (Type III), what is the primary reason one yields glass having fewer metal oxide impurities than the other? (Metal oxide impurities means cations other than silicon.)

Note: This exercise and others to follow are not for class discussion, but could be considered as useful homework.

Type IV

Plasma Torch

- A vapor phase oxidation process.
- Silica precursors enter in a dry (water vapor-free) gas stream.
- Again, a single-step boule process.
- Deposition rates greater than 0.5 gram/min are obtainable.

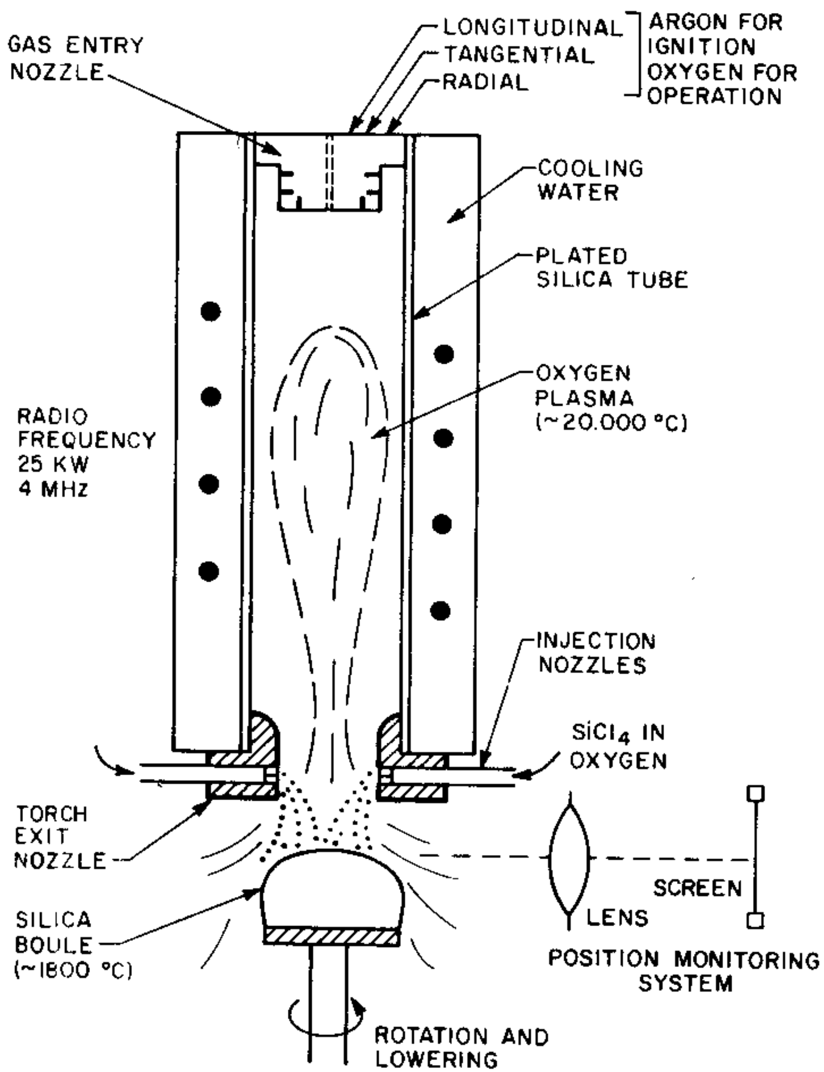


Fig. 2. Plasma torch arrangement for the production of fused SiO_2.

From Nassau and Shiever, 1975

Innovation Dates
Dry Synthetic Fused Silica

- Synthesis in water-free environment (hydrogen-free flame)
  - J.A. Winterburn
    - » U.S. Patent 3,275,408 (1966)
- Commercial Use of Plasma Torch for Bulk Silica Glass (e.g., Heraeus-Amersil, Thermal Syndicate Ltd., Thermal American Fused Quartz, Toshiba, Quartz et Silice)

Summary - Silica Glass - Type IV

- Synthetic
- Vapor phase oxidation of $SiCl_4$ or other precursor in plasma torch (water free)
- Silica "soot" collected and sintered on boule
- "Dry" - < 20 ppm OH
- Other impurities similar to Type III
- Examples:
  - Suprasil W (Heraeus)
  - Spectrosil WF (TSL)

Two-Step Flame Hydrolysis (Soot Re-melting)

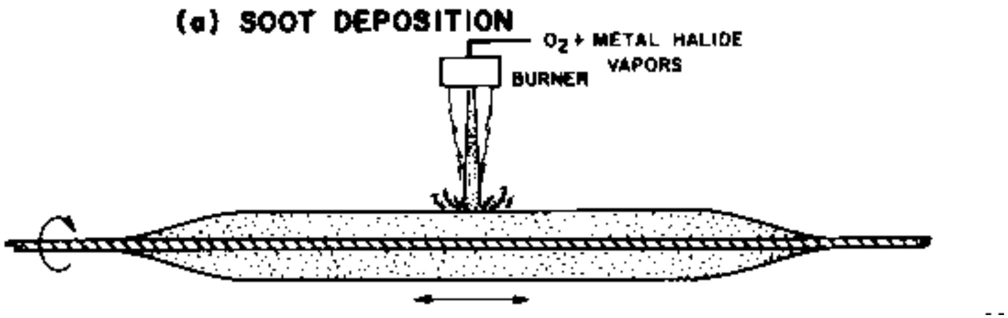
Fused Silica (Type IVa)

- Synthetic - Two steps – Sometimes called “soot re-melting” process
  - 1 - Deposition of a porous preform (at temperatures too-low for viscous sintering) wherein all the pores are interconnected and open to the surface.
    - » Pore size is typically about 0.3 μm (300 nm)
    - » Porosity about 75%
  - 2- Drying and consolidating the preform under flow of gases
    - » Typically Cl, for drying
    - » And He or vacuum for rapid, pore free sintering

- Very “Dry” - OH measured in ppm (< 10 ppm possible)
- Very pure – metal ion impurities measured in ppm

- Glass manufactured this way fits neither the Type III or Type IV category. I am arbitrarily calling it Type IVa.

Corning HPFS® Codes 7979 & 8655

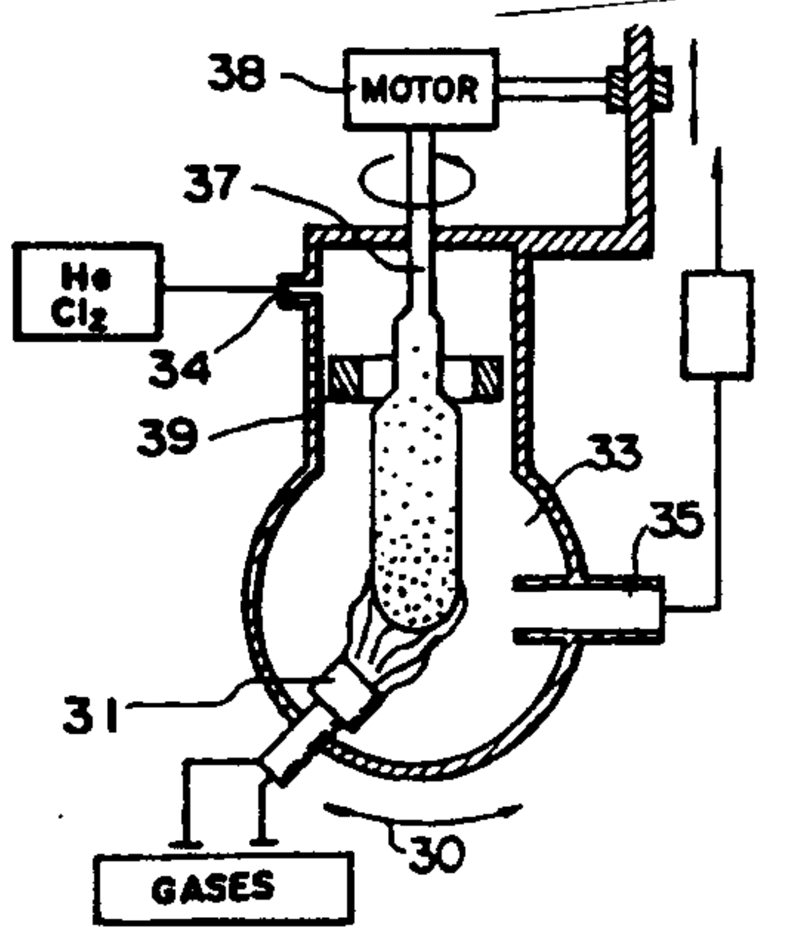


- This is a two-step soot re-melting process.
- First, the soot is laid down as a mechanically stable, partially sintered porous body, on a rigid mandrel.
- Second, the soot is dried and "consolidated" to full density in helium (rapidly diffusing gas) or vacuum atmosphere, with drying agents such as chlorine or carbon monoxide.
- The glass is then removed from the mandrel and worked into the desired shape, such as a flat slab.
- Process can be operated either horizontally or vertically.
- Can be scaled up by use of multiple burners.

Shin-Etsu VAD

- Shin Etsu (Japan), with Heraeus, has patented a process to conduct the two steps continuously, called Vapor Axial Deposition (VAD).
- Again, a boule process.

FIG. 5



Summary - Silica Glass - Type IVa

- Synthetic
- Flame hydrolysis of $SiCl_4$ or other precursor in oxy-fuel burner (usually oxygen + natural gas)
- Silica "soot" collected as a porous preform (on rotating mandrel or some other surface)
- Dried with flowing gases
- Sintered (consolidated) into boule with helium gas or vacuum.
- Examples:
  - » Corning HPFS 7989 and 8655

Innovation Dates
Synthetic Fused Silica (Vapor Phase Deposition)

- Flame hydrolysis
  - J.F. Hyde (Corning) - 1934
    - » U.S. Patent 2,272,342 (1942)
- Description of two-step process
  - M.E. Nordberg (Corning)
    - » U.S. Patent 2,326,059 (1943)
- Doped silica by flame hydrolysis
  - R.H. Dalton and M.E. Nordberg (Corning)
    - » U.S. Patent 2,239,551 (1941)
    - » U.S. Patent 2,326,059 (1943)
- Doping by impregnation of porous preform
  - Dumbaugh & Schultz
    - » U.S. Patent 3,864,113 (1975)

Innovation Dates
Synthetic Fused Silica, continued

- Invention of VAD Process, NTT (1977)
  - T. Izawa et al.
    - » U.S. Patent 4,062,665 (1977) and others
- Commercial Use of VAD for bulk silica
  - Heraeus Quartzglas, GmbH and Shin-Etsu Quartz Products
  - S Yamagata et al.
    - » U.S. Patent 5,325,230 (1994) and others
- Fused silica having low OH levels via two-step process
  - R.R. Khrapko et al.
    - » U.S. Patent 8,062,986 (2011)

Sol-Gel Type V

Fused Silica Type V
Sol-Gel Route

- Discussed in detail in Lectures 7 and 8 by Dr. Lisa Klein
- Preferred process used for Type V (1970s to present)
  - “Fumed” silica soot or other colloidal starting material
  - Stabilized as sol, cast, converted to gel, dried and sintered
- Applications
  - Lightweight space mirror blanks (Corning)
  - Optical components (Corning, Seiko)
  - Optical fiber outer cladding (AT&T/Lucent)

Exercise

- Do you agree the two-step soot re-melting process does not fit into either the Type III or Type IV classification?
- Why or why not?
- Should it have a classification of its own other than Type IVa?

Change of Direction
Adding Other Chemical Species to Synthetic Silica Glass

Adding Other Chemical Species to Silica Glass

- Question: Why go the trouble to make a high-purity silica only to add an "impurity" back in?

- Answer: For certain applications, (for examples optical fiber or very low expansion materials) very specific chemical additions are needed to provide the desired properties. They are often referred to as "dopants." Other impurities will detract from the desired properties or behaviors.

- So how do we "dope" silica?

- We will discuss several methods.

Doping of Fused Silica

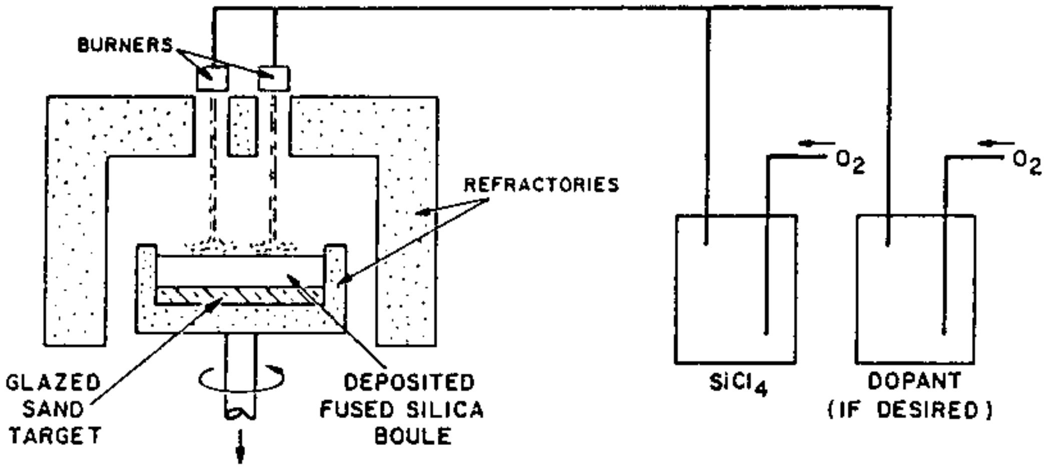


FIG. 10. Fused silica boule formed by simultaneous soot deposition and sintering in a flame oxidation furnace.

From Schultz and Scherer, 1983

Al_2O_3, ZrO_2, Nb_2O_5, Ta_2O_5, MoO_3, TiO_2, some 3d transition elements and a few others have been incorporated into Type III fused silica boules via this method. (Because of high vaporization rates, GeO_2, P_2O_5 and B_2O_3 are best added using the two-step process, Type IVa).

ULE^{TM} Titania & Silica

- Ultra-Low-Expansion ULE^{TM} (Corning Code 7971)
  - TiO_2 - doped fused silica (~ 7.5 wt% TiO_2), $TiCl_4$ precursor.
  - Made like synthetic fused silica Type III, one-step process.
  - Much poorer UV transmission than pure silica.

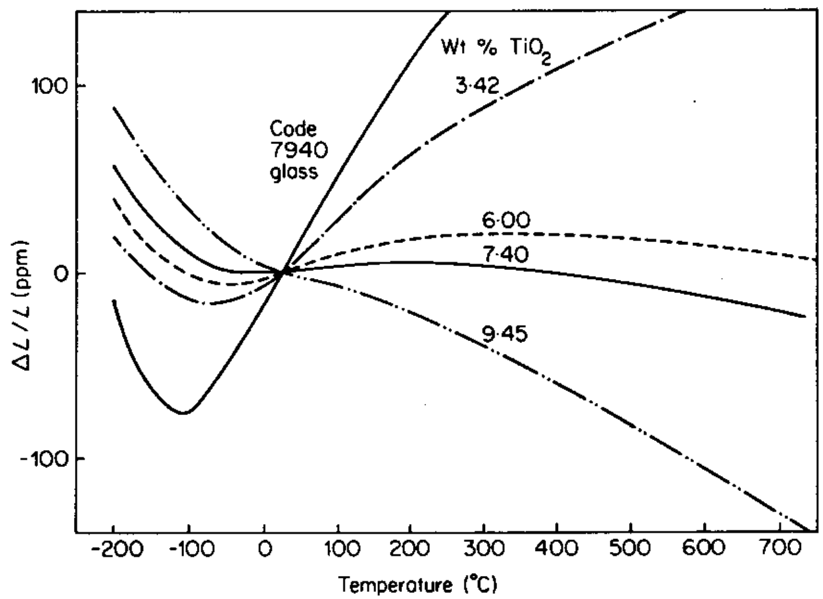


Figure 2. Thermal expansion of annealed vitreous silica and SiO_2–TiO_2 glasses

Plots of thermal expansion, not the expansion coefficient (slope of the lines).

<u>Properties:</u> Thermal expansion near zero from 5 °C to 35 °C, thus can be fusion sealed (welded) at room temperature enabling complex structures of extreme dimensional stability to be fabricated.

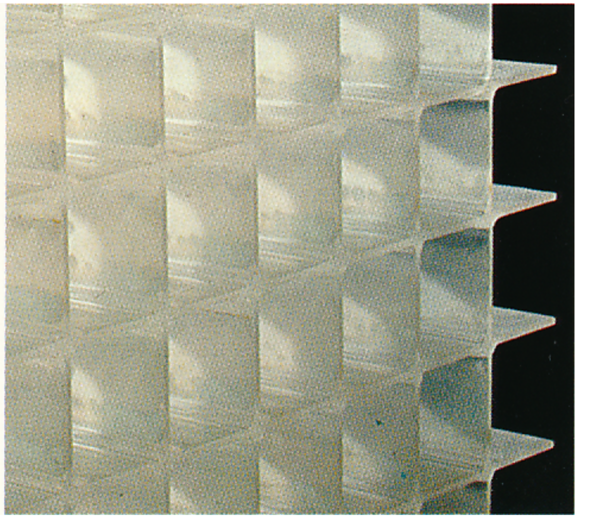
<u>Note:</u> Negative thermal expansion is observed at low temperatures, even for Corning Code 7940 fused silica.

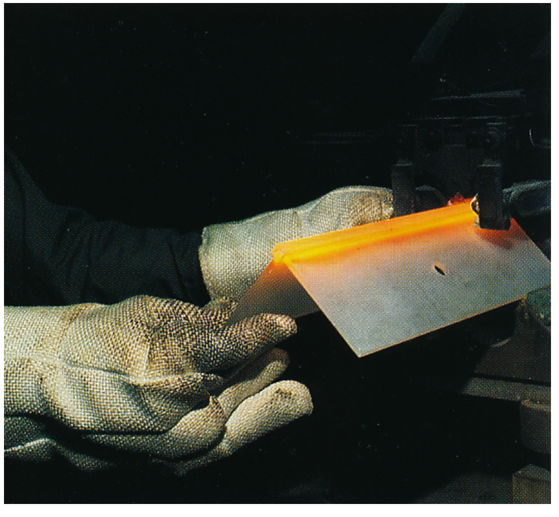
Fusion Sealing of ULE^{TM}

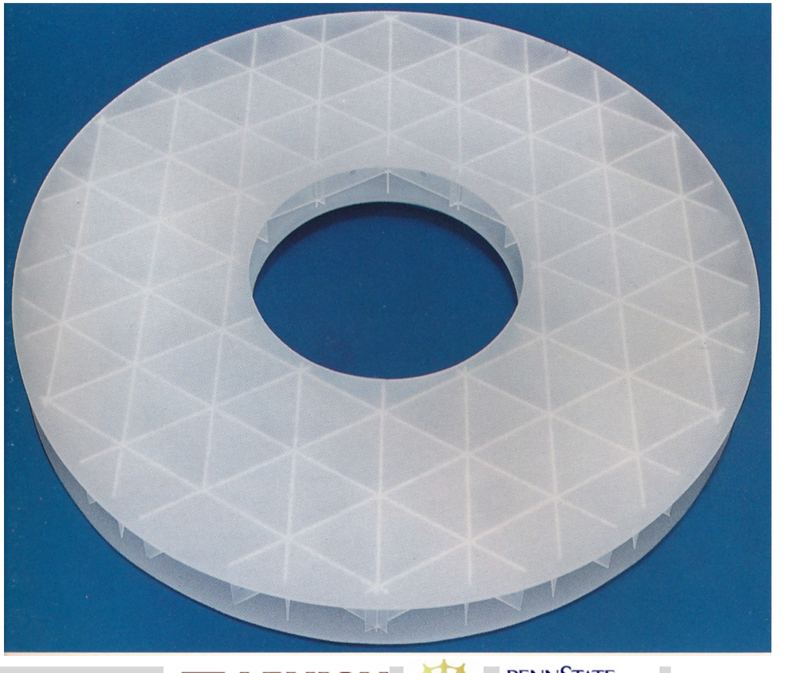
- Low thermal expansion allows fusion sealing (welding) of parts with negligible thermal shock.

- Complex, light-weight objects possible.

- Minimal annealing required.







Corning Incorporated Product Literature

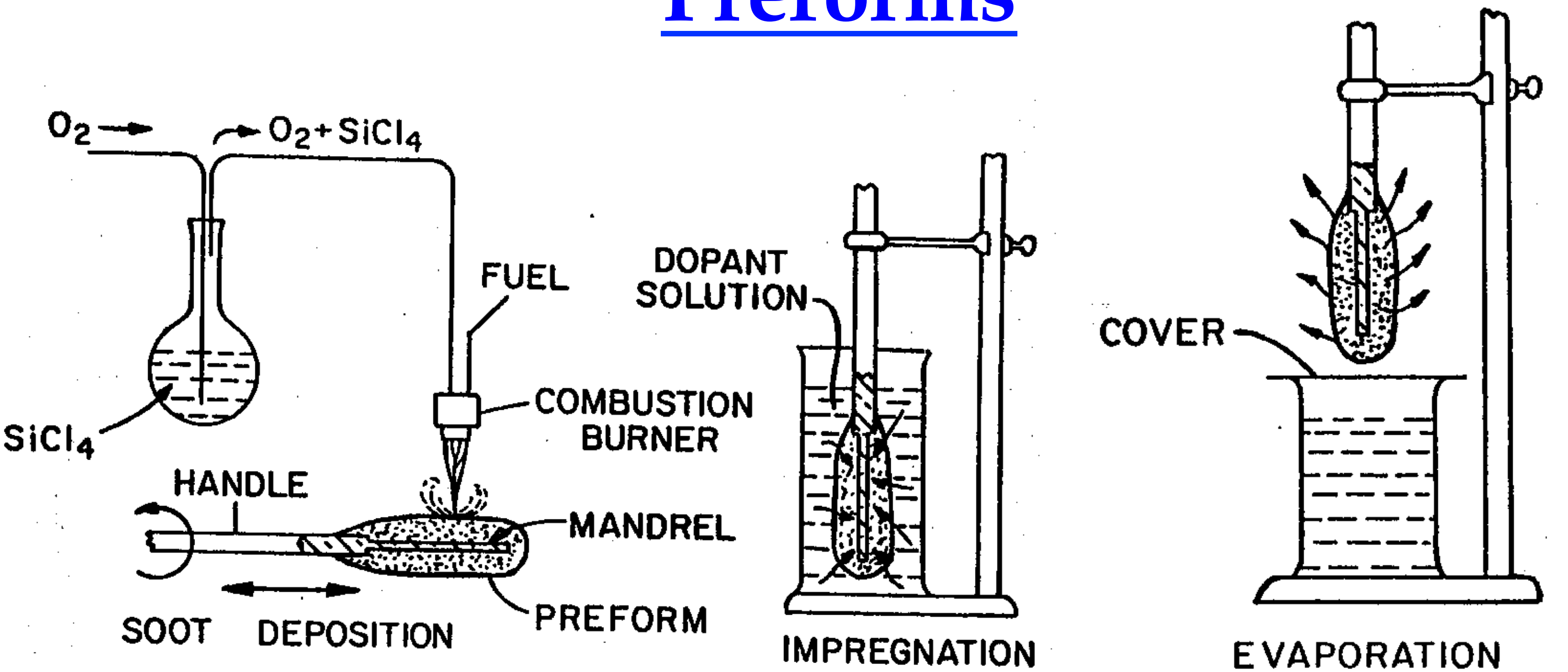
Ultra Low Expansion ULE™ (Corning Code 7971)

Hubble Space Telescope

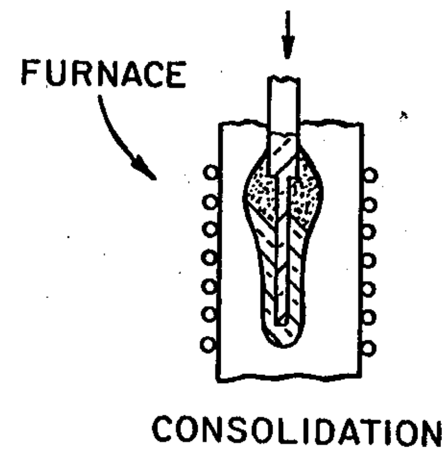
- Applications: telescope mirrors, light weight mirrors (for space), EUV microlithography stepper camera mirrors, precision athermal mountings and stages.

Corning Incorporated Product Literature

Impregnation Method of Doping Preforms



- The dopant is dissolved in a suitable volatile carrier.
- After evaporation, the adsorbed dopant becomes uniformly distributed within the glass during consolidation.



P.C. Schultz, US Patent 3,859,073, 1975

Type III and IVa Silica Applications

Diverse Silica Applications

- Examples
  - Earth- and space-based telescopes
  - Space vehicle windows
  - Microlithography stepper cameras and mirrors (for integrated circuit manufacture)
  - Optical Communications Fiber
    - » Introduction only
    - » Will be discussed further by the next lecturers

Reflecting Telescopes

Large Silica-based Optics: Earth-based telescopes

- Need:
  - To see further into space
  - Study weaker signals
- Mirror implications (theoretical):
  - Larger aperture (8 meter diameter or greater or multiple mirrors)
  - Greater angular resolution
  - Shorter focal lengths; F/2 or less
  - Parabolic shape
- Low thermal expansion
- Low thermal mass (as important as low thermal expansion)

Mirror Implications (practical):

- Other materials requirements:
  - Rigid, stable (no creep)
  - Capable of excellent polish (< 100 nm rms.)
  - Excellent chemical durability
  - Available in large sizes
  - Economically affordable

Recent Mirror Example Corning Incorporated

- Size - 8 m class
- Meniscus Type (mechanically supported thin mirror substrate)
- Material - ULE^{TM} titania-doped silica
- Hex-seal process, followed by thermal “sag” to shape
- Example: Suburu (Japanese National Large) Telescope, Mauna Kea, Hawaii

Spacecraft Windows

Comments on Spacecraft Windows

- Spacecraft windows used in in the space shuttle and earlier orbiting vehicles must survive severe environments:
  - High level of mechanical stress (pressure, shock, vibration)
  - High level of thermal stress
  - Abrasion from airborne particles

- The windows consist of three panes:
  - Inner pressure pane – Code 1723 high strain point, thermally tempered aluminosilicate glass (CTE ~ $45 \times 10^{-7}/^{o}C$)
  - Outer thermal pane – Code 7940 Type III fused silica (CTE ~ $5.5 \times 10^{-7}/^{o}C$)
  - Intermediate "redundant" pane – Code 7940 fused silica

- UV radiation absorption provided by the pressure pane composition and UV reflective coatings on the pressure and redundant panes.

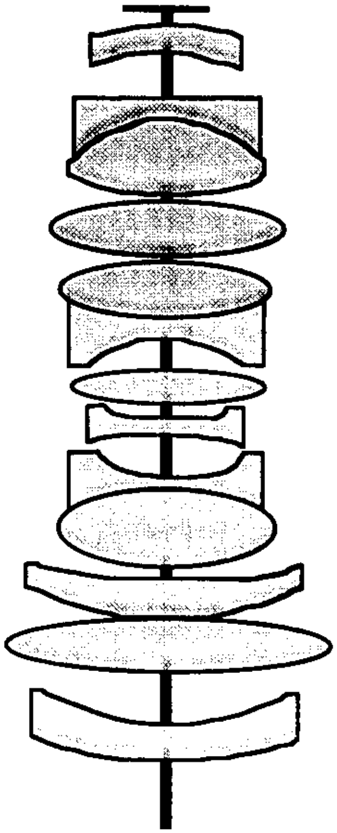
UV Optics

UV Optics

- Applications:
  - Microlithography stepper camera lenses and photo mask substrates for semiconductor industry
  - Laser fusion optics
- Materials:
  - Fused silica
  - Fluoride crystals and glasses
- Materials challenges:
  - Optical quality
  - Required sizes
  - High UV transmittance
  - Low laser damage

Glass Requirements for Microlithography Stepper Camera Lenses

- Operating at 248 nm and 193 nm excimer laser wavelengths
- Internal transmittance (through 1 cm glass at 193 nm)
  - 99%, preferred >99.5%
- Refractive index homogeneity
  $\Delta n < 2 \times 10^{-6}$
  gradient $< 0.1 \times 10^{-6}$
- Birefringence
  < 2 nm/cm



Example lens arrangement in stepper camera lens barrel

Stoichiometry and Impurity Defects

- Non-Stoichiometry
  - Oxygen excess or deficiency (network defects)
- Dissolved molecular hydrogen (H_2)
  - Generally found in "wet" synthetic silica
  - Conc. ~ 10^{17} to 10^{18} molecules/cm^3
- Dissolved chlorine
- Important for understanding and controlling certain laser radiation-induced effects such as transmission loss (darkening) and dimensional changes (either compaction or swelling) during product use.
- Need to minimize the compaction and swelling effects (ppm) prompted move from Type III to dry Type IVa glass for 193 nm lens applications.

Glass Requirements for Microlithography Stepper Camera Mirror Optics

Need for faster microprocessors and more memory per chip requires smaller features on chip and shorter wavelength optics to produce them.

- Industry is moving to EUV (extreme UV, wavelengths < 120 nm)
- Transmissive optics (lenses) no longer workable; all oxide glasses are essentially opaque at these wavelengths.
- Front surface mirrors are used for EUV
- Excellent transmission is no longer important
- But thermal expansion is.
- Heating of mirror will change shape and distort image unless CTE is extremely small.
- Therefore an important application for ULE™ glass.

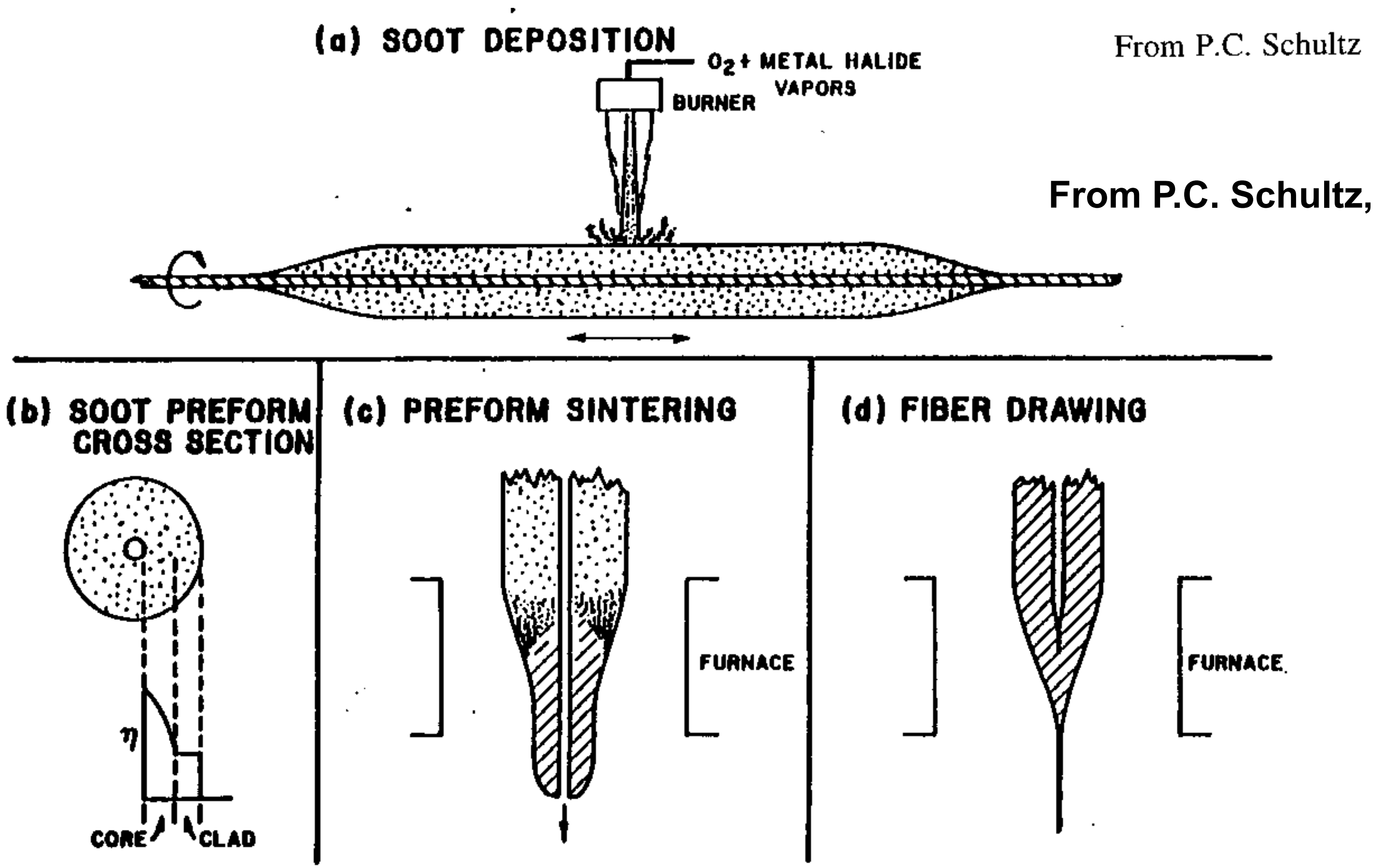
Optical Fiber for Telecommunications

Brief Introduction

- Optical fiber will be the subject of the next two lectures.
- However, the fiber manufacturing processes are based on the principles and understanding gained working with Types III and IVa fused silica and are deserving of a brief introduction here.

Corning OVD Process for Optical Fiber

From P.C. Schultz, 1979



OVD – Outside Vapor Deposition

Many layers (hundreds) deposited. Composition of vapor stream varied as a function of radius to provide the refractive index gradient.

IVPO / IVD Process for Optical Fiber

From P.C. Schultz

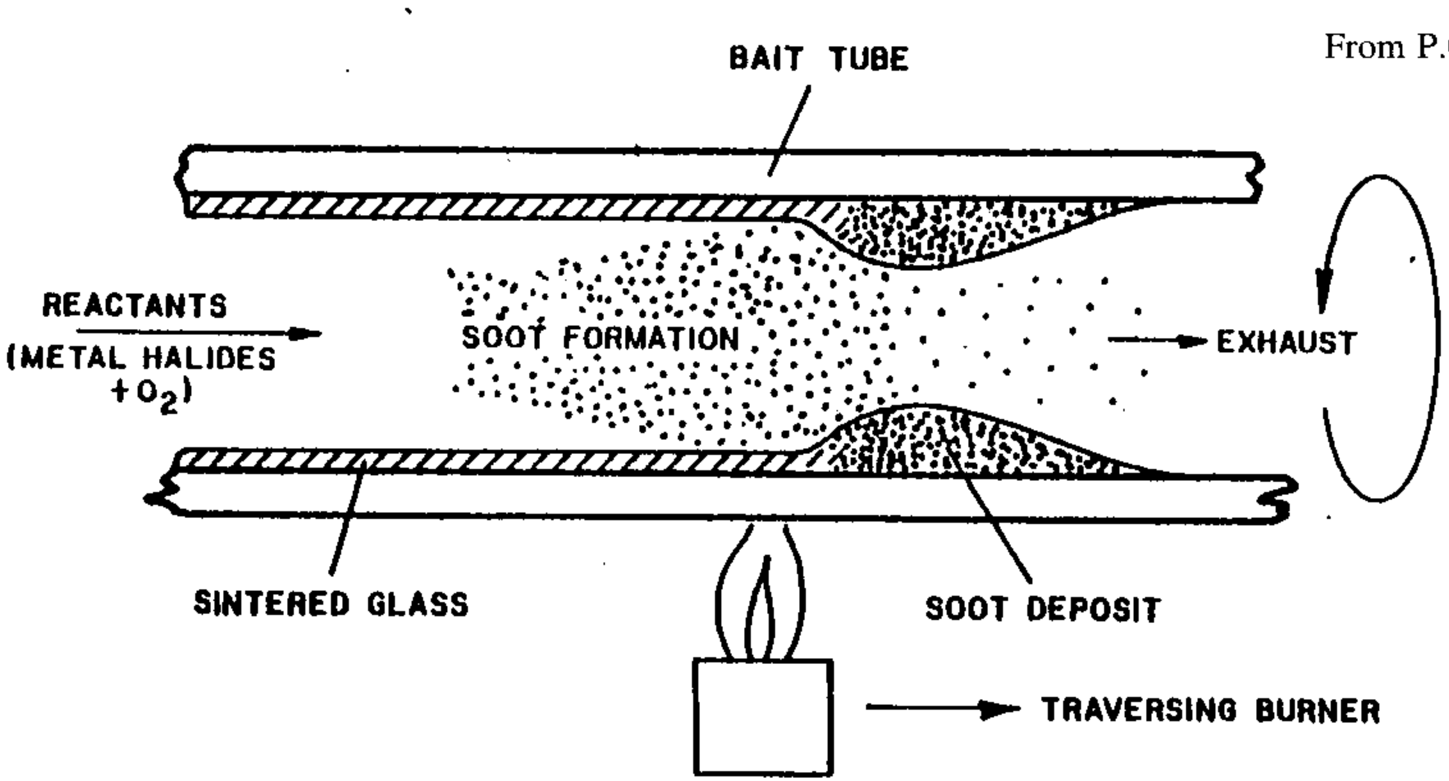


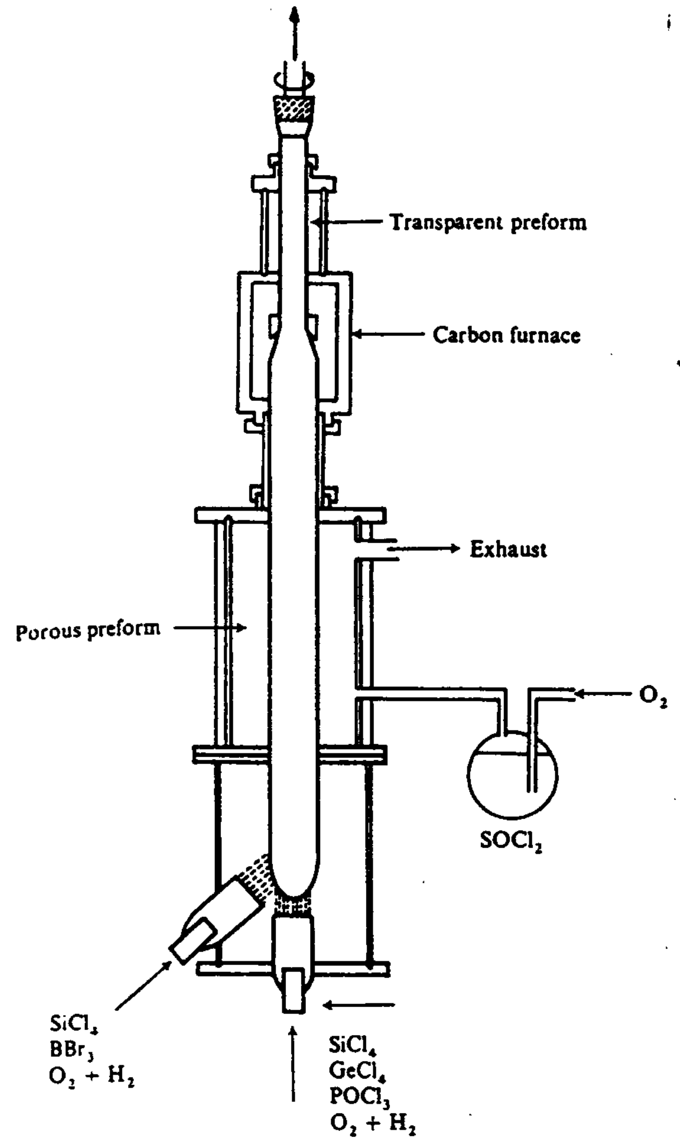
Figure 12. IVPO cross section.

From P.C. Schultz, 1979

IVPO – Inside Vapor Phase Oxidation or IVD – Inside Vapor Deposition
An oxidation process. No H_2O produced in the reaction.

VAD Process for Optical Fiber

- VAD – Vapor Axial Deposition
- Continuous process
- Soot deposited by two burners, each conveying a different combination of chemical streams to provide a refractive index gradient.
- Drying in separate chamber using flowing Cl_2, $SOCl_2$ or other gases.
- Consolidating at higher temperatures.



From K.J. Beales and C.R. Day – 1980
S. Sudo et al. - 1978

Key Innovation Dates - Synthetic Fused Silica for Optical Fiber

- First 20dB/km optical fiber (Corning) - 1970
- "Outside" process patented (Corning)
  - D.B. Keck, P.C. Schultz & F. Zimar
    - » U.S. Patent 3,737,292 (1973)
- "Inside" process (Corning)
  - D.B. Keck & P.C. Schultz
    - » U.S. Patent 3,711,262 (1973)

Vapor Phase Deposition Terminology

- All the vapor phase reaction (synthetic) processes discussed in these lectures involve a vapor phase reaction of chemical species in the presence of heat.
- Conventional CVD (chemical vapor deposition) involves a heterogeneous nucleation step whereby the reactions are initiated on a heated substrate and proceed to deposit a continuous film, coating, or just islands on that substrate.
- The processes we have discussed involve homogeneous nucleation in the vapor phase. The condensed particles are eventually collected on a substrate (or not), but the reaction does not occur there. They are technically not CVD processes. This is an important distinction.
- AT&T refers to the IVD process as MOCVD (Modified CVD)

Exercise

- For any one of the applications discussed (not including optical fiber), explain why no other glass composition, oxide or otherwise, is likely meet the requirements. You may base your answer on physical properties or other factors.

Acknowledgements

- Various editions of *The Encyclopedia of Chemical Technology*
  - W. Winship; W.H. Dumbaugh and P.C. Schultz; P.S. Danielson; D.R. Sempolinski and P.M. Schermerhorn
- *Glass Science and Technology, Vol. 1*
  - P.C. Schultz and G. Scherer
- *Commercial Glasses (Adv. in Ceramics 18)*
  - P. P. Bihuniak
- P.C. Schultz, Applied Optics 18, 3684-3995 (1979).
- C.L. Rathmann, G.H. Mann and M.E. Nordberg, Applied Optics 7, 819-823 (1958).
- Various U.S. and international patent publications.