

"METHOD OF PREPARING A SILICA GLASS MEMBER"

This invention relates to a method of preparing a silica glass member.

Silica glass is used for many purposes such as glass wafers, semiconductor industrial material, optical material, preforms for optical fibres, a support tube and a photo mask substrate, and thus the demand for silica glass is expected to expand more and more in the future.

So far as the method of preparing silica glass at a low cost is concerned, the sol-gel method has been proposed. For example, this method is disclosed in "Journal of Non-Crystalline Solids" Vol. 37, No. 191 (1980) by Nogami et al, "Journal of Non-Crystalline Solids", Vol. 47, No. 435 (1982) by Rabinovitch et al, U.S. Patent Application Serial No. 642,606 by Toki et al (corresponding to British Patent Specification No. 2,140,408 and U.S. Patent Application Serial No. 826,527 by Matsuo et al (corresponding to British Patent Specification No. 2,170,799.

The difference between the various methods referred to in the above literature concern the components of the sol solution which is to be the main material, and the methods can be classified into the following four groups:-

1) The use of a sol obtained by hydrolyzing a mixture solution of alkyl silicate, water, alcohol and an appropriate catalyst such as hydrochloric acid, ammonia and so on (Nogami's method)

2) The use of a mixture sol obtained by mixing

⊙.....excellent
 ○.....good
 Δ.....satisfactory
 X.....unsatisfactory.

5 So far as mass production is concerned, Toki's method is
 the best of the above four methods, and so far as the physical
 properties of the product in terms of high purity are concerned,
 Matsuo's method is the best of the above four methods.

10 However, when a sol as described above is used
 as the starting material and is only dried and sintered,
 there are many inclusions in the silica glass member so obtained.
 In order to enhance the quality of the glass, Matsuo et al
 have succeeded in removing any inclusions which are larger
 than a few microns, by using a clean environment, by irradiating
 15 the sol with supersonic waves in order to improve
 the dispersion properties by filtering, and by centrifugal
 separation. Matsuo et al have also succeeded in preventing
 bubbling by closing the pores in the dry gel as a result
 of sintering in an He atmosphere or under reduced pressure.
 20 The inclusions in the silica glass have been substantially
 reduced by this method. However, it has not so far been possible
 to produce silica glass which does not include silica crystals,
 inclusions, micro-cracks, bubbles and so on. The silica glass
 which is presently available still cannot be used in any
 25 field where very high quality is required, such as in the
 production of a photo mask substrate and a preform for an
 optical fibre.

a solution of alkyl silicate hydrolyzed with an acid reagent and a solution including fine particle silica obtained by hydrolyzing alkyl silica with a basic reagent at a predetermined mixing ratio (Matsuo's method).

5

3) The use of a mixture sol obtained by mixing a solution of alkyl silicate hydrolyzed with an acid reagent and ultra fine particle silica at a predetermined mixing ratio (Toki's method), and

10

4) The use of a sol obtained by diffusing ultra fine particle silica into water or an organic solvent at a predetermined ratio (Rabinovitch's method).

15

The resulting sol prepared by each method as mentioned above is gelled in a container of the desired shape and the resulting dry gel is sintered to yield silica glass. Each of the methods as mentioned above has merits and demerits of its own, and the features of each method are shown in the following table.

	Nogami	Matsuo	Toki	Rabinovitch
Purity of the silica glass	⊙	⊙	△	△
Cost of raw material	○	△	○	⊙
Yield	×	⊙	⊙	○
Size	×	⊙	⊙	△
Mass-productivity	×	△	⊙	○

The symbols employed in the above Table have the following meanings:

According, therefore, to the present invention, there is provided a method of preparing a silica glass member, comprising the steps of:

5 drying a sol containing silica and/or a silica precursor so as to form a dry gel,

obtaining a glass or a glass precursor member by removing gas from said dry gel and closing pores in said dry gel, and

10 obtaining a silica glass member by heating said glass or glass precursor member to a selected temperature in the range between 1500 and 2200°C and maintaining the said glass or glass precursor at said temperature.

15 The invention enables a silica glass member of optically high quality to be produced which can be used as a photo mask substrate or as a preform for an optical fibre. In addition, the present invention enables the mass-production of silica glass and also the moulding of silica glass to be improved.

20 The sol may be obtained by hydrolyzing alkyl silicate with water and with an acid or basic reagent.

Alternatively, the sol may be obtained by mixing together a solution of alkyl silicate hydrolyzed with an acid reagent and a solution including particulate silica

obtained by hydrolyzing alkyl silicate with a basic reagent.

5 A further possibility is that the sol is obtained by mixing together a solution of alkyl silicate hydrolyzed with an acid reagent and particulate silica.

Furthermore, the sol may be obtained by diffusing particulate silica into water or into an organic solvent.

Preferably the particulate silica has a mean particle diameter between 0.01 and 1.0 microns.

10 The pores in the said dry gel may be closed by sintering said dry gel in an He atmosphere sintering the dry gel under a reduced pressure, or sintering the dry gel under a reduced pressure after the dry gel has been exposed to an He atmosphere.

15 A gas burner may be used for heating said glass or glass precursor member to the said selected temperature.

The glass or glass precursor member may be heated to the said selected temperature by means of a high temperature furnace having a graphite, a tungsten or
20 a molybdenum heating element.

Alternatively, the glass or glass precursor member may be heated to the said selected temperature by means of a high temperature continuous heat-treating furnace.

The glass or glass precursor member may be heated to the said selected temperature by means of a high temperature gas furnace in which the combustion of hydrogen or a hydrocarbon gas is used as a heat source.

5 Spacer means may be provided between the glass or glass precursor member and a support therefor.

 The said spacer means may be constituted by carbon powder, carbon fibres or paper-like or fabric-like material obtained by processing carbon fibres.

10 The said spacer means may alternatively be constituted by a powder which is hard to sinter. Thus the said powder may be alumina, zirconia, or silicon nitride.

 A number of said glass or glass precursor members may be simultaneously heat-treated while mounted on said
15 spacer means.

 The said glass or glass precursor member or members may be moulded by using a casting of desired configuration, when said glass or glass precursor member is heated to the said selected temperature.

20 Alternatively, the glass or glass precursor member or members may be moulded to a desired configuration by subjecting the said member to an external force when said glass or glass precursor member is heated to the said selected temperature.

Preferably, after the glass or glass precursor member has been heated to the said selected temperature, it is cooled to room temperature in a plurality of stages, the cooling rate being smaller in at least one of said stages than in another stage or stages thereof.

One of the merits of the sol-gel method is that a high melting point glass can be synthesized at a low temperature. In fact, if the silica glass is manufactured by the fusing method, a very difficult manufacturing step at a temperature higher than 1700°C is necessary. On the other hand, if the silica glass is manufactured by the sol-gel method, it is easy to manufacture the glass at a low temperature of about 1200°C .

The temperature of vitrification depends upon the components of the sol which is the starting material and, for example, when alkyl silicate is hydrolyzed with an acid reagent or with a basic reagent, the temperature of vitrification is 900°C and 1200°C , respectively. When the solution obtained by hydrolyzing alkyl silicate with the acid reagent is mixed with fine particle silica obtained by hydrolyzing alkyl silicate with the basic reagent or with ultra fine particle silica, although the temperature of vitrification also depends upon the mixing ratio thereof, the vitrification is completed at a temperature lower than 1400°C . The

temperature of vitrification is highest when a sol solution is used in which ultra fine particle silica is diffused into the solvent, but even in this case the vitrification is completed at a temperature less than 1470°C.

The use of the sol-gel method, therefore, enables the silica glass to be manufactured with less energy in comparison with that required in the fusing method.

However, there are some inclusions, defects and so on in the silica glass manufactured by the sol-gel method whatever may be the components of the sol solution. These defects arise from:-

1) Inorganic matter, for example, dust mixed in the raw material and the sol solution,

2) Defects produced by the burning out of the organic inclusions,

3) Micro-cracks occurring at the time of shrinking,

4) Bubbles or blow holes included at the time of gelation or produced during the sintering step,

5) Silica crystals produced during the sintering step (mainly, cristobalite), and

6) Silica-coagulated material which is insufficiently sintered.

In the case of the present invention the glass or glass precursor member which may be obtained by the conventional sol-gel method is heated to a temperature close to the melting point of silica and thus the glass or glass precursor is brought temporarily to the half-fusing phase. The crystals mentioned in (5) above and the silica-coagulated material mentioned in (6) above disappear at a temperature higher than that of silica, and even if the temperature is lower than the fusing temperature, an almost uniform silica glass is produced. Moreover, the defects of (2), the micro cracks of (3) and the bubbles of (4) and so on disappear during the process of sintering by heating the dry gel to the high temperature if the pores in the dry gel are closed in an He atmosphere or under reduced pressure.

The inorganic matter of (1), even if the melting point is higher than that of silica, disappears optically during the process of sintering by heating the dry gel to a temperature close to the melting point of silica, because the interface of (1) and the silica glass disappears and the composition of the glass is made uniform. However, when extremely large particles, or inorganic materials which are hard to vitrify, are included, the quality of the glass is not made completely uniform. It is desirable to remove particles whose size is larger than a few microns

by performing the sol processing in a clean environment and also by filtering or centrifugal separating.

Since the melting point of silica is 1713°C , if this temperature or one higher is maintained in the manufacturing process, the high quality of the silica glass is assured. So far as improving the quality is concerned, there is an adequate improvement at a temperature of 1500°C or higher. Accordingly, the high temperature treatment employed in the present invention starts at a temperature of at least 1500°C in view of the quality required, the consumption of energy and the characteristics of the furnace. However, since too high a temperature causes violent vaporization of the silica, the upper limit of the temperature is substantially 2200°C .

As mentioned above, the present invention is applicable regardless of the components of the sol. However, unless the pores of the dry gel are closed, the pores grow into very large bubbles. The pores may be closed by one of the following methods:

- 1) sintering and closing pores in the dry gel in an He atmosphere,
- 2) sintering and closing pores in the dry gel under reduced pressure, and
- 3) sintering and closing pores in the dry gel under reduced pressure after the dry gel has been exposed to an He atmosphere.

In the step of closing pores in the dry gel, it is not always necessary to completely vitrify the dry gel but this can be done if a translucent glass precursor is obtained. There may be several methods for heating a glass or glass precursor member, after closing the pores to a selected temperature between 1500 and 2200°C.

First, use may be made of a gas burner of hydrogen, acetylene and so on. The gas burner is easily available and the operation thereof is easy. However, it has some disadvantages in that the control of the temperature is very difficult and the difference between the temperature of the surface and that of the inside of the glass is considerable. Moreover, this method is not suitable for mass-production.

Second, use may be made of a high temperature furnace in which graphite, tungsten, molybdenum or the like is used as the heating element. This, however, is very expensive and its operation is difficult in that, for example, this furnace is used in the atmosphere where there is no oxygen. However, an accurate temperature control is assured and high quality silica glass can be manufactured with a stable yield. Furthermore, the high temperature furnace can also be used as a high temperature continuous heat-treating furnace by combining the heating elements, which is useful for mass production.

Besides the above, a high temperature gas oven may be used in which the combustion of hydrogen or hydrocarbon gas is used as the heat source.

In the production of a photo mask substrate, a
5 wide square of, for example, 5 inch (12.7cms) x 5 inch
(12.7 cms) x 0.09 inch (0.23 cms) or 6 inch (15.24 cms)
x 6 inch (15.24 cms) x 0.12 inch (0.30 cms) is required
in addition to stable quality. To satisfy both of these
requirements, a high temperature furnace may be employed
10 in which graphite, tungsten or molybdenum is used as
the heating element. However, since the samples are treated
in the half fused state, the samples are liable to be
welded to the furnace material, thereby causing, cracks
and transformation. Therefore, it is desirable to provide
15 an isolating layer between the furnace material and the
samples to avoid the cracks and transformation.

Since carbon material is chemically very stable
in an inert atmosphere, it does not react on the silica
glass, thereby making it easy to obtain a material of
20 high purity. If an isolating layer of powder or fibres
is used, the difference between the expansion coefficients
of the samples and of the furnace material is absorbed by
the displacement of the isolating layer, thereby preventing
the cracks and the transformation. Moreover, even though
25 a part of the isolating layer of carbon powder or carbon

fibres adheres to the sample, it is easy to remove it by washing or burning. If carbon processed to a paper-like or fabric-like shape is used as the isolating layer, the handling becomes much easier and the state of the contact surface becomes better. If an isolating layer is provided between one sample and another, the same effect as mentioned above is obtained, and space in the furnace is substantially improved, so that mass production is made easier.

10 If a high temperature furnace is employed in which tungsten or molybdenum or the like is used as the heating element, then if there is carbon present, the heating element tends to become carbonized and accordingly deteriorates. Therefore, in such a case, powder which is
15 hard to sinter, such as alumina, zirconia, silicon nitride or the like could be used as the isolating layer. However, any powder which adheres to the sample is hard to remove.

 If the glass or glass precursor member is heated to
20 the selected temperature between 1500 and 2200°C, the sample becomes soft and easily transforms. One of the merits of the sol-gel method is the ease with which the product maybe moulded at the time of gelation. Furthermore, it is also possible to mould the gel
25 during the high temperature treatment. For example,

when a large square silica glass plate is to be manufactured, its flat shape is not always maintained during vitrification even if the gelation is carried out in a container such as a flat plate casting. When the sample is placed on a furnace plate having a flat surface and is heated to the high temperature, the sample is flattened by its own weight. This makes it suitable for subsequent grinding.

If a casting of a desired configuration, whether flat or not, is used, an extremely precise moulding can be produced. It is also possible to apply pressure to the samples by a press device provided in the furnace instead of depending upon the weight of the sample itself.

If a silica glass rod or a tube is to be manufactured, it would be more efficient to use a ring burner or a ring heater. When the central portion of the rod or tube is heated to the high temperature with both ends of the rod or tube fixed, by subjecting both ends to tension, the straightness of the rod or tube is improved.

The method mentioned above is very important when the invention is used in connection with the production of the preform and the support tube of an optical fibre.

If the glass or glass precursor member is heated to the selected temperature between 1500 and 2200°C and cooled down rapidly, the internal stress remains in the silica glass. Therefore, either the cooling down

after the high temperature treatment may be gradual or there may be annealing after rapid cooling. Thus, in the manufacturing process of the glass, at least one step of cooling down the material gradually from 1200°C to room temperature should be included.

The high temperature treatment according to this invention is basically different from the fusing method. The major differences between the present invention and the fusing method are as follows:- the bulk of the silica glass itself has been already moulded by the sol-gel method of the prior art, the length of the high temperature treatment being even less than that of the fusing method and almost no work is required at the time of high temperature treatment. A heat-treatment is similar to an annealing treatment to remove distortion in glass, and therefore, this is regarded as a treatment for removing inclusions in the glass. As explained above, according to the present invention, an improved silica glass member of high quality and high mouldability, which cannot be manufactured by the prior art sol-gel method, can be produced. Further, the present invention provides such a silica glass at a lower cost than in the prior art.

Furthermore, a multicomponent series glass such as, for example, an alkali-proof glass of the $\text{SiO}_2\text{-ZrO}_2$ series or a low thermal expansion coefficient glass of the

$\text{SiO}_2\text{-TiO}_2$ series may also be provided with high quality and at low cost by the use of the present invention.

5 As previously indicated, an optically high quality silica glass which can be used as a photo mask substrate and as a preform for an optical fibre can be supplied at a low cost in large quantities.

The invention is illustrated by the following Examples.

10 Example 1

440ml of ethyl silicate and 360ml of 0.05 normal hydrochloric acid solution were mixed together and stirred violently to yield a water-like transparent uniform solution. The pH of the solution so obtained was adjusted to 4.2 with 0.1 normal ammonia water and then the solution was filtered through a filter having holes whose diameter was 1 micron. 500ml of the resulting solution was poured into a container made of polypropylene (whose dimensions were 20cms in width, 20 cms in length and 10cms in height). The solution was gelled and dried for ten days at a temperature of 60°C in the said container which was covered with a lid with openings amounting to 0.5% of the surface area of the lid, thereby obtaining a water-like transparent dry gel.

25 The dry gel was placed in a gas displacement furnace

and the temperature thereof was raised to 700°C at a heating rate of 30°C per hour. When the temperature became 700°C, pure helium gas was introduced in an amount of 1l/min into the furnace, the temperature
5 was raised to 900°C at a heating rate of 10°C per hour and the dry gel was maintained at 900°C for one hour. As a result, the dry gel was made into a clear glass member whose specific gravity was 2.20. The size thereof was 8cm x 8cm x 0.5cm. Only a few inclusions in the member
10 having a diameter of a few microns were detected.

By use of a gas burner, an oxy-hydrogen flame was applied to both sides of the silica glass member so obtained. When the temperature of the surface of the silica glass member was at least 1800°C, the silica
15 glass member was maintained for more than ten seconds at this temperature and the whole surface thereof was heated to an almost uniform condition. As a result, no inclusions were detected by a microscope having a magnification of 100, although the whole surface exhibited
20 distortions. After the silica glass member had been maintained at 1200°C for one hour, the temperature was lowered at a cooling rate of 100°C per hour in order to remove the distortions. The silica glass member so obtained was mirror-polished into a glass member of 2mm
25 in thickness and then collimated light from a lamp was

directed onto it so that the illumination was 50,000 lux in a dark room. However, there were no reflectance points.

Example 2

5 440ml of ethyl silicate, 900ml of ethanol and 360ml
of 0.1 normal ammonia water were mixed uniformly and
were maintained for one day at room temperature. The
resulting emulsion sol was concentrated to 440ml
10 in total volume by using a rotary evaporator. The said
sol was filtered by means of a filter having
holes whose diameter was 1 micron, and 440ml of the
resulting solution was poured into a container (of 5cm
inside diameter, and 30cm depth) made of polypropylene
having a lid with openings amounting to 2% of the surface
15 area of the lid. After the solution had been dried
at 60°C for ten days, a white dry gel was obtained.

 The dry gel so obtained was placed in a vacuum
furnace and the temperature was raised to 900°C at
a heating rate of 60°C per hour. The atmospheric pressure
20 in the vacuum furnace was lowered to less than 1 Torr
by using a rotary pump and then, while maintaining the
pressure, the temperature was raised to 1200°C at a
heating rate of 100°C per hour. After the dry gel was
maintained at the temperature of 1200°C for one hour,
25 a vitrification of the dry gel occurred. The specific
gravity thereof was 2.20 and a silica glass rod was
obtained, the diameter and length thereof being 2.5cm

and 10cm, respectively. When the silica glass rod was exposed to the irradiation of laser light whose wavelength was 0.633 μ m, the light was scattered everywhere.

5 The rod was fixed on a glass lathe and was heated by an oxy-hydrogen flame while rotating. When the surface temperature was at least 2000°C, the rod was maintained at this temperature for at least 30 seconds and then the rod was heated uniformly by sliding the burner along it. When laser light was directed onto the silica glass rod
10 again, no scattering of the light was observed.

Example 3

440ml of the ethyl silicate, 900ml of the ethanol and 360ml of 0.1 normal ammonia water were mixed uniformly and were maintained for one day at room temperature.
15 After the resulting emulsion sol had been concentrated to 440ml in total volume by using a rotary evaporator, the pH thereof was adjusted to 4.0 by adding 1.0 normal hydrochloric acid solution.

Separately from the above, a water-white transparent
20 uniform solution was obtained by violently stirring a mixture of 440ml of ethyl silicate and 360ml of 0.05 normal hydrochloric acid solution. This solution was uniformly mixed with the sol obtained above and was then filtered by means of a filter having
25 holes whose diameter was 1 μ m. The pH of the solution was adjusted to 4.8 with 0.1 normal ammonia water

and then 1,000ml of the resulting solution was poured into a container made of TEFLON (Registered Trade Mark), the container being 6cms inner diameter and 40cm length and being sealed with a stopper. After setting the sol in the container on a revolving
5 device and rotating the container about the central axis of the said device at a rotational speed of 500rpm for one hour, the container was left at rest for two days.

After taking off the stopper of the container, the dry gel was removed from the latter and placed in another container
10 (10cm width, 45cm length, 15cm height) made of polypropylene which was then covered with a lid, the latter having openings amounting to 1% of the surface area of the lid. When the dry gel was dried at 60°C for ten days, a tubular dry gel was obtained.

The tubular dry gel was placed in a vacuum furnace and was
15 heated to 800°C at a heating rate of 60°C per hour. After the atmospheric pressure in the vacuum furnace had been lowered to 1 Torr or less at the temperature of 800°C, pure helium gas was passed over the gel at 1l/min in the furnace.

The atmospheric pressure in the vacuum furnace was lowered to
20 1 Torr or less again and then, while maintaining this pressure, the temperature of the vacuum furnace was raised to 1200°C at a heating rate of 100°C per hour. After the dry gel had been maintained at the temperature of 1200°C for one hour, the dry gel was vitrified. The specific gravity thereof was 2.20 and the
25 product was in the form of a silica glass tube whose outer diameter, inner diameter and length were 3cm, 1cm and 20cm, respectively. When this silica glass tube was exposed to irradiation by laser light whose wavelength was 0.633μm, the light was scattered everywhere.

The silica glass tube was placed in a graphite heating furnace vertically and after the introduction of N_2 gas in substitution for the original atmosphere, the temperature therein was raised to $1600^{\circ}C$ in two hours and was maintained at this temperature for ten minutes. The temperature was then lowered to $1200^{\circ}C$ at the rate of $1000^{\circ}C$ per hour and was then further lowered to room temperature at the rate of $100^{\circ}C$ per hour. When the silica glass tube was exposed to irradiation by laser light, very little scattering of the light was observed.

Example 4

440ml of ethyl silicate and 360ml of 0.05 normal hydrochloric acid solution was mixed together and stirred violently to obtain a water-like transparent uniform solution. 150g of ultra fine particle silica (Aerosil OX-50) was added little by little to the water-like transparent uniform solution and the solution was stirred sufficiently. This sol was exposed to irradiation by ultrasonic waves of 28KHz for two hours at a temperature of $20^{\circ}C$, and after a centrifugal force of 1500G was applied for ten minutes to remove large particle silica, the sol was filtered by means of a filter having holes whose diameter was 1 micron.

The pH of the highly homogeneous sol obtained above was adjusted to 4.2 with 0.1 normal

ammonia water. 500ml of the resulting solution was poured into a container (20cm width x 20cm length x 10cm height) made of polypropylene having a lid whose openings amounted to 1% of the surface area of the lid.

5 When this sol solution was dried at a temperature of 60°C for seven days, a white and porous dry gel was obtained.

The dry gel was placed in a gas displacement furnace and heated to 1000°C at the rate of 60°C per hour. When the temperature became 1000°C, pure helium
10 gas at a flow rate of 1l/min was introduced into the furnace and the dry gel was heated to 1300°C at the rate of 30°C per hour. When the dry gel was maintained at 1300°C for one hour, the vitrification of the dry gel was completed and a silica glass plate was obtained whose specific
15 gravity was 2.20. The size of the silica glass plate was 10cm x 10cm x 0.5cm. Inclusions and β cristobalite crystals whose diameter was about 10 micron were detected to a small extent in the silica glass plate.

Carbon powder was placed on a graphite plate
20 (15cm x 15cm x 1cm) to a depth of about 1mm. The silica glass plate was mounted on the carbon-covered graphite plate and this assembly was placed in a graphite heating furnace. After the furnace atmosphere had been replaced by N_2 gas, the temperature therein was raised to
25 1800°C in two hours and was maintained at this temperature

for ten minutes. The temperature was then lowered to 1200°C at a cooling rate of 1000°C per hour and was then further lowered to room temperature at a cooling rate of 100°C per hour.

5 There was no fusion between the graphite plate and the silica glass plate and the flatness of the silica glass was excellent. The silica glass plate so obtained was mirror-polished into a plate of 2mm thickness and then the collimated light from a lamp was directed onto it
10 so that the intensity of the illumination was 50,000 lux in a dark room. However, no reflectance points were detected. Optically, a very high quality silica glass without crystals or distortion was obtained.

Example 5

15 250g of ultra fine particle silica (Aerosil 200) was scattered into 500ml of pure water and this sol or slurry was exposed to irradiation by ultrasonic waves of 28KHz for two hours at a temperature of 20°C. 400ml of the slurry which had a high viscosity, was poured into a
20 container (5cm inner diameter, 30cm depth) made of polypropylene and having a lid with openings amounting to 2% of the surface area of the lid. When this slurry was dried at 60°C for ten days, a white and porous dry gel was obtained.

25 This dry gel was placed in a gas displacement

furnace and heated to 1100°C at the rate of 60°C per hour. When the temperature became 1100°C , pure helium gas was introduced into the furnace at a flow rate of 1l/min , and the dry gel was heated to 1400°C at the rate of 30°C per hour. When the dry gel was maintained at 1400°C for one hour, although the silica glass precursor rod which was so obtained was translucent, the specific gravity thereof was 2.20.

The silica glass precursor rod was placed in a high-temperature gas furnace vertically, and heated to 1800°C by a propane gas flame and was maintained at this temperature for ten minutes. The temperature was then lowered to 1200°C at the rate of 1000°C per hour and was then further lowered to room temperature at the rate of 100°C per hour.

As a result a transparent silica glass rod was obtained without blowholes. The diameter and length of the transparent silica glass rod were 4cm and 24cm, respectively. When the transparent silica glass rod was exposed to the irradiation of laser light whose wavelength was $0.633\mu\text{m}$, no scattering of the light was observed.

Example 6

Zirconia powders were laid on a tungsten plate ($15\text{cm} \times 15\text{cm} \times 0.2\text{cm}$) so that the thickness thereof was about 1mm. A silica glass plate obtained by closing the pores in the dry gel by the same method as in Example 4 was placed thereon and the assembly was introduced

into a tungsten heating furnace. After the furnace atmosphere had been replaced by N_2 gas, the temperature therein was raised to $1800^{\circ}C$ in two hours and maintained at this temperature for ten minutes. The temperature was then lowered to $1200^{\circ}C$ at a cooling rate of $1000^{\circ}C$ per hour, and was then further lowered to room temperature at a cooling rate of $100^{\circ}C$ per hour.

The tungsten plate was not fused with the silica glass plate and the flatness of the silica glass plate was excellent. The silica glass plate obtained above was mirror-polished to provide a plate of 2mm thickness and then collimated light from a lamp was directed onto it so that the intensity of illumination was 50,000 lux in a dark room. However, no reflectance points were detected. Optically, a very high-quality silica glass member without crystals or distortion was obtained.

Example 7

1760 ml of ethyl silicate, 2690ml of ethanol and 670ml of 1.0 normal ammonia water were mixed uniformly and were maintained for five days at room temperature. After 400ml of pure water had been added to the resulting emulsion, the sol was concentrated to 1000ml in total volume by using a rotary evaporator. The pH of the sol was also adjusted to 4.0 by adding 2.0 normal hydrochloric acid solution.

Separately from the above, a water-like transparent uniform solution was obtained by stirring violently a mixture of 760ml of ethyl silicate and 250ml of 0.02 normal hydrochloric acid solution. The resulting solution was uniformly mixed with the sol obtained above, and then filtered by a filter having holes whose diameter was 1 micron. After the pH of the solution had been adjusted to 4.2 with 0.1 normal ammonia water, a centrifugal force of 1500 G was applied for ten minutes to remove large particle silica.

The resulting solution was then filtered again by means of a filter having holes whose diameter was 1 micron.

1100ml of the resulting sol having a high degree of homogeneity was poured into a container (30cm x 30cm x 15cm) height made of polypropylene, the container having a lid with openings amounting to 0.5% of the surface area of the lid. When this sol was dried at a temperature of 60°C for twenty days, a white and porous dry gel was obtained (22cm x 22cm x 0.9cm).

The resulting dry gel was placed in a gas displacement furnace and dry air was caused to flow over it at a flow rate of 2l/min. The dry gel was heated to 700°C at the rate of 60°C per hour and maintained at 700°C for twenty hours. Helium gas, instead of the dry air, was introduced into the furnace at a flow rate of 2l/min, and then the

dry gel was maintained at 900°C, 1000°C, 1100°C and 1200°C for ten hours respectively. Vitrification of the dry gel was thus completed and the size and the flatness thereof were such as to yield a silica glass plate of 15.5cm x 15.5cm x 0.6cm, and 2mm respectively.

Carbon paper, (e.g. KUREHA carbon fibre paper) as thick as 0.3mm was laid on a graphite plate (20cm x 20cm x 1cm). The silica glass plate was mounted thereon and the assembly was placed in a graphite heating furnace.

After the furnace atmosphere had been replaced by N₂ gas, the temperature therein was raised to 1850°C in two hours and maintained at this temperature for five minutes. The temperature was then lowered to 1200°C at a cooling rate of 1000°C per hour and further, lowered to room temperature at a cooling rate of 100°C per hour.

The graphite plate was not fused with the silica glass plate and the flatness of the silica glass plate was accurate to 0.1mm or less. The silica glass plate which was so obtained was mirror polished into a plate of 6 inch (15.24 cms) x 6 inch (15.24 cms) x 0.12 inch and 0.3 cms and then collimated light from a lamp was directed onto it so that the intensity of illumination was 50,000 lux in a dark room. However, no reflectance points were detected. When the transmittance of ultraviolet light through the silica glass plate was measured, for a wavelength

of 200nm or more, the transmittance was constantly 90% or more and no specific absorption was observed.

Example 8

1150ml of ethyl silicate and 620ml of 0.01 normal hydrochloric acid solution were mixed together and stirred violently to obtain a water-like transparent uniform solution. 300g of ultra fine particle silica (Reolosil QS-102) were added little by little to the above solution with stirring and this sol was exposed to irradiation by ultrasonic waves of 28KHz for two hours at a temperature of 20°C. After a centrifugal force of 1500G had been applied for ten minutes to remove the large particle silica, the sol was filtered by means of a filter having holes whose diameter was 1 micron. After the pH of the resulting solution was adjusted to 4.2 with 0.1 normal ammonia water, the centrifugal force of 1500G was applied again for ten minutes and the sol was filtered by means of a filter having holes whose diameter was 1 micron.

1100ml of the resulting sol having a high degree of homogeneity was poured into a container (30cm width and 30cm length x 15cm height) made of polypropylene having a lid provided with openings amounting to 0.5% of the surface area of the lid. When this sol was dried at a temperature of 60°C for 20 days, a white and porous dry gel was obtained.

The dry gel was placed in a gas displacement furnace and dry air was introduced into the furnace at a flow rate of 2ℓ/min. In the course of being heated to 700°C at the rate of 60°C per hour, the dry gel was maintained at 200°C, 300°C and 500°C for three hours, respectively. Helium gas was then introduced instead of the dry air at a flow rate of 2ℓ/min and then the resulting dry gel was maintained at 700°C, 900°C, 1000°C, 1100°C and 1200°C for ten hours, respectively. Vitrification of the dry gel was thus completed so as to produce a silica glass plate whose specific gravity was 2.20.

Carbon paper as thick as 0.3mm was laid on a graphite plate (20cm x 20cm x 1cm). The silica glass plate was mounted thereon and the assembly was introduced into a graphite heating furnace which was heated to 1800°C. After the resulting silica glass plate was maintained at this temperature for ten minutes, the silica glass plate was moved into a cold chamber and cooled to room temperature in 30 minutes. Since distortion was found in the silica glass plate, the silica glass plate was heated to 1200°C and maintained at 1200°C for one hour and then the temperature was lowered at the rate of 100°C per hour in order to remove the distortion. The flatness thereof was accurate to less than 0.1mm.

The resulting silica glass plate was mirror-polished into a plate of 6 inch x 6 inch x 0.12 inch, and then collimated light from a lamp was directed onto it so that the intensity of illumination was 50,000 lux in the dark room. However, no reflectance points were detected. When the transmittance of ultraviolet light through the silica glass plate was measured for a wavelength of 200nm or less, the transmittance was constantly 85% or more and no specific absorption was observed.

Example 9

A white and porous dry gel (22cm x 22cm x 0.9cm) obtained by using the same method as in Example 7 was placed in a gas displacement furnace and dry air was introduced into the furnace at a flow rate of 2l/min. The temperature in the furnace was raised to 700°C at the rate of 60°C and was maintained at the temperature of 700°C for 20 hours. Helium gas instead of the dry air was introduced into the furnace at a flow rate of 2l/min, and then the temperature in the furnace was maintained at temperatures of 800°C, 900°C and 1000°C for five hours, respectively. When the temperature had fallen to room temperature, a white and porous dry sintering gel was obtained whose size was 18cm x 18cm x 0.7cm.

Carbon paper of a thickness up to 0.3mm was laid on a graphite plate (20cm x 20cm x 1cm) and the said

sintering gel obtained by heating to the 1000°C was mounted thereon, the assembly being placed in a graphite heating furnace. While maintaining a reduced pressure of not more than 1 Torr in the furnace by using a rotary pump, the temperature in the furnace was rapidly raised to 1000°C in ten minutes. The temperature was then raised to 1300°C at a heating rate of 300°C per hour and was maintained at the temperature of 1300°C for one hour. At this temperature, N_2 gas was introduced into the furnace continuously, the temperature therein being raised to 1750°C at a heating rate of 600°C per hour and maintained at the latter temperature for 30 minutes.

The resulting transparent silica glass plate was moved into a cold chamber and chilled to room temperature in 30 minutes. The transparent silica glass plate whose size was 15.5cm x 15.5cm x 0.6cm which was so obtained had no observed fractures or cracks. Since distortion was found in the silica glass plate, the silica glass plate was heated to 1200°C and maintained at 1200°C for one hour and then the temperature was lowered at the rate of 100°C per hour in order to remove the distortion.

The resulting silica glass plate was mirror-polished into a plate of 6 inch x 6 inch x 0.12 inch and then collimated light from a lamp was directed onto it so that the intensity of illumination was 50,000 lux in a dark room.

However, no reflectance points were detected. Optically a very high-quality silica glass plate was obtained without crystals and distortion. When the transmittance of ultraviolet light through the plate was measured, for the wavelength of 200nm or more, the transmittance was constantly 90% or more and no specific absorption was observed.

Example 10

Ten pieces of silica glass (15.5cm x 15.5cm x 0.6cm) obtained by closing pores in the dry gel on an He atmosphere according to the same method as in Example 7 were prepared. Five pieces of carbon paper whose size was 17cm x 17cm x 0.93cm and five silica glass plates were arranged alternately on a graphite plate of 20cm x 20cm x 1cm. The graphite plate was mounted on four graphite props whose height was 4cm. Further, five silica glass plates and five pieces of the carbon paper were mounted alternately thereon in the same way as described above. In this way, the ten pieces of silica glass were set in position. After the furnace atmosphere had been replaced by N₂ gas, the various silica glass plates were moved into a graphite heating furnace having a temperature of 1800°C and were maintained therein for fifteen minutes. The silica glass plates were then moved into a cold chamber and cooled to room temperature in 30 minutes.

There was no fusion either between the graphite plate and the silica glass plates or between the silica plates themselves. The flatness of each silica glass plate was accurate to less than 0.2mm. Since distortion was found in the plates, the latter were maintained at 1200°C for one hour and then the temperature was lowered at the rate of 100°C per hour in order to remove the distortion.

Each of the resulting silica glass plates was mirror-polished into a plate of 6 inch x 6 inch x 0.2 inch, and then collimated light from a lamp was directed onto it so that the intensity of illumination was 50,000 lux in the dark room. However, no reflectance points were detected. Optically very high-quality silica glass plates without crystals or distortion were obtained. When the transmittance of ultraviolet light through the plates was measured, for a wavelength of 200nm or more, the transmittance was constantly 90% or more and no absorption was observed.

Example 11

2200ml of ethyl silicate and 1600ml of 0.02 normal hydrochloric acid solution were mixed together and stirred violently to obtain a water-like transparent uniform solution. 600g of ultra fine particle silica (Aerosil OX-50) was added little by little to the water-like

transparent uniform solution and the solution was stirred sufficiently. This sol was exposed to irradiation by ultrasonic waves of 28 KHz for two hours at a temperature of 20°C, and after a centrifugal force of 1500 G was applied for ten minutes to remove large particle silica, the sol solution was filtered by means of a filter having holes whose diameter was 1 micron. After the pH of the resulting solution had been adjusted to 4.8 with 0.1 normal ammonia water, the sol was filtered by means of a filter having holes whose diameter was 1 micron.

3770ml of the highly homogeneous sol solution obtained above was poured into a container (6cm inner diameter, 150cm length) such as an aluminium tube coated with TEFLON (Registered Trade Mark) and the container was sealed with a stopper. After setting the sol in the container on a revolving device and rotating the container about its central axis at a rotational speed of 500rpm for one hour, the container was left at rest for four days at room temperature. After taking off the stopper, the tubular gel within the container was removed therefrom and placed in another container (10cm x 170cm x 20cm height) made of polypropylene. The latter container had a lid whose openings amounted to 0.5% of the surface area of the lid, the above-mentioned gel being dried therein at 60°C for 30 days, whereby a tubular dry gel was obtained.

The said tubular dry gel was placed in a gas displacement furnace and dry air was introduced into the latter at a flow rate of 2ℓ/min. The temperature in the furnace was raised to 700°C at the rate of 60°C per hour and was maintained at this temperature for ten hours. A gas mixture comprising helium (1.8ℓ/min) and chlorine (0.2ℓ/min) was introduced into the furnace instead of the dry air therein, and then the temperature in the furnace was raised to 1000°C at the rate of 30°C per hour. O₂ gas was introduced into the furnace at a flow rate of 2ℓ/min instead of the said gas mixture, and then the tubular dry gel was maintained at temperatures of 1000°C and 1050°C for ten hours, respectively.

Finally, He gas (2ℓ/min) instead of the O₂ gas was introduced into the furnace, and then the tubular dry gel was maintained at temperatures of 1050°C, 1100°C and 1200°C for ten hours, respectively. Although the resulting silica glass precursor member was translucent, the specific gravity thereof was almost 2.20, while the outer diameter, inner diameter and length were 3cm, 1cm and 75cm, respectively. The degree of ovality of the silica glass precursor member was 0.1% and the bow was 2.0mm/m.

The silica glass precursor member so obtained above was fixed at both ends in a vertical disposition and was moved into a ring heater in which graphite was the

heating element. While the argon gas was caused to flow around the ring heater, the temperature therein was maintained at 2000°C. The silica glass precursor member was moved so that the upper end was moved at the rate of 3cm/min and the lower end was moved at the rate of 4cm/min to the vertical direction. Next, the resulting silica glass member was placed in an electric oven and after the silica glass member was maintained for one hour therein at a temperature of 1200°C, the temperature was lowered at a cooling rate of 100°C per hour to remove the distortion. The outer diameter, inner diameter and length thereof were 2.6cm, 0.87cm and 1m, respectively. Although the degree of ovality was 0.1% again, the bow was improved to 0.1mm/m.

When the silica glass member was exposed to irradiation by laser-light whose wavelength was 0.633μm, no scattering of the light was observed. Moreover, when the water content of the silica glass member was measured by measuring its absorption of 2.72μm wavelength light, it was less than 1ppm.

Example 12

440ml of ethyl silicate and 360ml of 0.05 normal hydrochloric acid solution were mixed together and stirred violently to obtain a water-like transparent uniform solution. 150g of the ultra fine particle silica (Aerosil OX-50) were added little by little to the

water-like transparent uniform solution and the solution was stirred sufficiently. This sol was exposed to irradiation by ultrasonic waves of 28KHz for two hours at a temperature of 20°C, and after a centrifugal force of 1500G was applied for ten minutes to remove the large particle silica, the sol was filtered by means of a filter having holes whose diameter was 1 micron.

The pH of the highly homogeneous sol obtained above was adjusted to 4.2 with 0.1 normal ammonia water. 700ml of the resulting solution was poured into a container (30cm inner diameter, 10cm height) made of polypropylene and having a lid with openings amounting to 1% of the surface area of the lid. When this sol was gelled and dried at a temperature of 60°C for seven days, a white and porous dry gel was obtained.

The dry gel obtained above was placed in a vacuum furnace and the temperature was raised to 1000°C at the rate of 60°C per hour. The atmospheric pressure in the vacuum furnace was lowered to not more than 1 Torr by using a rotary pump and then, while maintaining the pressure, the temperature was raised to 1300°C at the rate of 100°C per hour. After the dry gel was maintained at the temperature of 1300°C for one hour, vitrification of the dry gel occurred. The diameter and the thickness thereof were 15cm and 0.5cm, respectively.

The silica glass plate so obtained was laid on a concave graphite member having a radius of curvature of 30 cms, and this assembly was placed in a graphite heating furnace. After the furnace atmosphere was replaced with N_2 gas, the temperature was raised to $1800^{\circ}C$ in two hours, and the temperature was maintained at this temperature for ten minutes. The temperature was then lowered to $1200^{\circ}C$ at a cooling rate of $1000^{\circ}C$ per hour, and the temperature was further lowered to room temperature at a cooling rate of $100^{\circ}C$ per hour. A uniform silica glass member whose shape was like a watch-glass was obtained. There were no blow holes and optically high quality silica glass was obtained.

Example 13

A silica glass plate (15cm diameter, 0.5cm thickness) was sintered in a vacuum furnace by the same method as in Example 1.2 and was introduced into a graphite crucible and heated therein. The silica glass plate was then placed in a graphite heating furnace having a hotpress mechanism. After the furnace atmosphere was replaced by N_2 gas, the temperature was raised to $1850^{\circ}C$ in two hours and this temperature was maintained for five minutes. After this, the silica glass plate was pressed to a pressure of 10kg/cm through graphite members, the temperature was lowered to $1200^{\circ}C$ at the rate of $1000^{\circ}C$ per hour, and was thereafter lowered to room temperature at the rate of $100^{\circ}C$ per hour.

An extremely high-quality silica glass member was obtained whose shape was like a crucible.

Example 14

5 A silica glass plate (15.5 cm x 15.5cm x 0.6cm) obtained by closing the pores in a dry gel in an He atmosphere by the use of the method of Example 7 was placed in an electric furnace and maintained at a temperature of 1600°C for 30 minutes. The temperature was lowered to 1200°C at a cooling rate of 1000°C per hour and further lowered
10 to room temperature at a cooling rate of 100°C per hour.

When the resulting silica glass plate was mirror-polished to form a plate of 6 inch (15.24 cms) x 6 inch (15.24 cms) x 0.12 inch (0.30 cms), collimated light from a lamp was directed onto it so that the intensity of illumination
15 was 50,000 lux in a dark room. The silica glass plate was then examined in this light to see whether there were any inclusions in the silica glass plate which would show up in the form of points of light. Some small points of lights were detected with the naked eye in the surface.

20 Example 15

A silica glass plate (15.5 cm x 15.5cm x 0.6cm) obtained by closing pores in a dry gel in an He atmosphere by the same method as Example 7 was placed in a graphite heating furnace. After the furnace atmosphere
25 was replaced by argon gas, the temperature was raised to 2100°C in two hours and was maintained at that temperature

for one minute. The temperature was lowered to 1200°C at a cooling rate of 1000°C per hour and was then further lowered to room temperature at a cooling rate of 100°C per hour.

5 The size of the silica glass plate was reduced to 14cm x 14cm x 0.5cm by vaporization of silica. The silica glass plate was mirror-polished to form a plate of 2mm in thickness and then collimated light from a lamp was directed onto it so that the intensity of illumination was 50,000 lux in a dark room. However, no reflectance points were detected.

10

The following three Examples, namely Examples 16-18, are not within the scope of the present invention and are given for comparison purposes only.

15 Example 16

A silica glass plate (15.5cm x 15.5cm x 0.6cm) obtained by closing pores in a dry gel in an He atmosphere by the same method as Example 7 was placed in a furnace and maintained at a temperature of 1450°C for 30 minutes.

20 When the temperature was lowered to room temperature, the surface of the silica glass plate became white by crystalization.

When the resulting silica glass plate was mirror-polished to form a plate of 6 inch (15.24 cms) x 6 inch (15.24 cms) x 0.12 inch (0.30 cms) collimated light was directed onto it

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so that the intensity of illumination was 50,000 lux in a dark room, a light spot was clearly visible. Moreover, reflectance points of various sizes were visible in the glass.

5 Example 17

A silica glass plate (15.5cm x 15.5cm x 0.6cm) obtained by closing pores in a dry gel by the same method as in Example 7 was placed in a graphite heating furnace. After the furnace atmosphere had been replaced with argon gas, 10 the temperature was raised to 2300°C rapidly and then lowered to room temperature. There was little silica glass left in the furnace.

Example 18

A white and porous dry gel obtained by drying by 15 the same method as in Example 4 was heated to 1300°C in the atmosphere so that a transparent silica glass plate was obtained whose size was 10cm x 10cm x 0.5cm. Inclusions whose diameter was about 10 microns and blow holes were detected in the plate. The silica glass plate was placed 20 in a graphite heating furnace. After this, the furnace atmosphere was replaced with N₂ gas and maintained at a temperature of 1800°C for ten minutes. Since violent bubbling occurred in the silica glass, the volume of the glass was increased threefold.

As mentioned above the present invention provides an improved silica glass member so far as its optical quality is concerned, the glass or glass precursor preferably being heated to 1500°C to 2000°C and maintained at this temperature for a predetermined period of time in the sol-gel method.

It is desirable to close the pores in the dry gel in an helium atmosphere under the reduced pressure in order to prevent bubbling. However, the present invention is not limited to a particular method of preparing the sol or a particular method of heating. Furthermore, this invention can be applied to articles of various shapes.

The present invention enables even silica glass made by the sol-gel method to be used not only for the silica substrate of an IC Mask or a support tube for optical communication fibres but also to be used for the mother rod for optical communication fibres, and so on.

C L A I M S

1. A method of preparing a silica glass member, comprising the steps of:

drying a sol containing silica and/or a silica precursor so as to form a dry gel,

5 obtaining a glass or a glass precursor member by removing gas from said dry gel and closing pores in said dry gel, and

obtaining a silica glass member by heating said glass or glass precursor member to a selected temperature in the range between 1500 and 2200°C and maintaining said glass
10 or glass precursor at said temperature.

2. A method as claimed in claim 1, wherein said sol is obtained by hydrolyzing alkyl silicate with water and with an acid or basic reagent.

3. A method as claimed in claim 1, wherein said sol is
15 obtained by mixing together a solution of alkyl silicate hydrolyzed with an acid reagent and a solution including particulate silica obtained by hydrolyzing alkyl silicate with a basic reagent.

4. A method as claimed in claim 1, wherein said sol
20 is obtained by mixing together a solution of alkyl silicate hydrolyzed with an acid reagent and particulate silica.



5. A method as claimed in claim 1, wherein said sol is obtained by diffussing particulate silica into water or into an organic solvent.
- 5 6. A method as claimed in any of claims 3-6 in which the particulate silica has a mean particle diameter between 0.01 and 1.0 microns.
7. A method as claimed in any preceding claim, wherein the pores in said dry gel are closed by sintering said dry gel in an He atmosphere.
- 10 8. A method as claimed in any of claims 1-6 wherein the pores in said dry gel are closed by sintering the dry gel under a reduced pressure.
9. A method as claimed in any of claims 1-6 wherein the pores in said dry gel are closed by sintering the dry gel under a reduced pressure after the dry gel has been exposed to an He atmosphere.
- 15 10. A method as claimed in any preceding claim, wherein a gas burner is used for heating said glass or glass precursor member to the said selected temperature.
- 20 11. A method as claimed in any of claims 1-9, wherein the glass or glass precursor member is heated to the said selected temperature by means of a high temperature furnace having a graphite, a tungsten or a molybdenum heating element.



* C L M S *

12. A method as claimed in any of claims 1-9, wherein the glass or glass precursor member is heated to the said selected temperature by means of a high temperature continuous heat-treating furnace.
- 5 13. A method as claimed in any of claims 1-9, wherein the glass or glass precursor member is heated to the said selected temperature by means of a high temperature gas furnace in which the combustion of hydrogen or a hydrocarbon gas is used as a heat source.
- 10 14. A method as claimed in claim 11 or 12, wherein spacer means are provided between the glass or glass precursor member and a support therefor.
- 15 15. A method as claimed in claim 14, wherein said spacer means is constituted by carbon powder, carbon fibres or paper-like or fabric-like material obtained by processing carbon fibres.
16. A method as claimed in claim 14 wherein said spacer means is constituted by a powder which is hard to sinter.
- 20 17. A method as claimed in claim 16 in which the said powder is alumina, zirconia, or silicon nitride.



18. A method as claimed in any of claims 14 to 17 wherein a number of said glass or glass precursor members are simultaneously heat-treated while mounted on said spacer means.
- 5 19. A method as claimed in any preceding claim, wherein said glass or glass precursor member is moulded by using a casting of desired configuration when said glass or glass precursor member is heated to the said selected temperature.
- 10 20. A method as claimed in any of claims 1-18 wherein said glass or glass precursor member is moulded to a desired configuration by subjecting said member to an external force when said glass or glass precursor member is heated to the said selected temperature.
- 15 21. A method as claimed in any preceding claim, wherein, after the glass or glass precursor member has been heated to the said selected temperature, it is cooled to room temperature in a plurality of stages, the cooling rate being smaller in at least one of said
- 20 stages than in another stage or stages.
22. A method of preparing a silica glass member substantially as described in any of the Examples 1-15.



* C L M S *

23. A silica glass member when made by the method of
any preceding claim.

