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DECISION
of 20 November 2003

Case Number: T 0574/01 - 3.3.5

Application Number: 96100119.5

Publication Number: 0720970

IPC: C03C 3/06

Language of the proceedings: EN

Title of invention:
Silica glass for photolithography, optical member including the same, exposure apparatus including the same, and method for producing the same

Patentee:
NIKON CORPORATION

Opponent:
Heraeus Quarzglas GmbH & Co.KG

Headword:
Silica glass/NIKON

Relevant legal provisions:
EPC Art. 100(b), 54, 56,

Keyword:
"Sufficiency of disclosure (yes)"
"Implicit lack of novelty (not shown)"
"Inventive step (yes)"

Decisions cited:
-

Catchword:
-

Case Number: T 0574/01 - 3.3.5

DECISION
of the Technical Board of Appeal 3.3.5
of 20 November 2003

Appellant: (Proprietor of the patent)	NIKON CORPORATION 2-3, Marunouchi 3-chome Chiyoda-ku Tokyo 100 (JP)
Representative:	Hansen, Bernd, Dr. Dipl.-Chem. Hoffman Eitle, Patent- und Rechtsanwälte Arabellastrasse 4 D-81925 München (DE)
Respondent: (Opponent)	Heraeus Quarzglas GmbH & Co.KG Quarzstrasse 8 D-63450 Hanau (DE)
Representative:	Staudt, Armin, Dipl.-Ing. Patentanwälte Grimm & Staudt Edith-Stein-Strasse 22 D-63075 Offenbach/M. (DE)
Decision under appeal:	**Decision of the Opposition Division of the European Patent Office posted 19 March 2001 revoking European patent No. 0720970 pursuant to Article 102(1) EPC.**

Composition of the Board:

Chairman:	M. M. Eberhard
Members:	B. P. Czech
	J. H. Van Moer

Summary of Facts and Submissions

I. The appeal is from the decision of the opposition division posted 19 March 2001 revoking European patent No. 0 720 970. The decision was based on the granted claims (main request) and on two sets of amended claims submitted on 12 January 2001 (first and second auxiliary requests).

II. The independent claims as granted read as follows:

"1. A silica glass for photolithography used together with light in a wavelength region of 400 nm or shorter, said silica glass having a structure determination temperature of 1,200 K or lower and an OH group concentration of at least 1,000 ppm."

"11. An optical member used together with light in a wavelength region of 400 nm or shorter, said optical member comprising a silica glass according to claim 1".

"13. An exposure apparatus using light in a wavelength region of 400 nm or shorter as exposure light, which comprises:

a stage allowing a photosensitive substrate to be held on a main surface thereof;

an illumination optical system for emitting the exposure light of a predetermined wavelength and transferring a predetermined pattern of a mask onto said substrate;

a projection optical system provided between a surface on which the mask is disposed and said substrate, for projecting an image of the pattern of said mask onto said substrate; and

an optical member comprising the silica glass according to claim 1."

"17. A method for producing a silica glass having a structure determination temperature of 1,200 K or lower and an OH group concentration of at least 1,000 ppm, said method comprising the steps of:
heating a silica glass ingot having an OH group concentration of 1,000 ppm or more to a temperature of 1,200 to 1,350 K;
maintaining said ingot at said temperature for a predetermined period of time; and then
cooling said ingot to a temperature of 1,000 K or lower at a temperature-lowering rate of 50 K/hr or less to anneal said ingot."

III. During the opposition proceedings, the following prior art documents had inter alia been cited:

E4: EP-A-0 401 845

E5: US-A-5 364 433

E7: EP-A-0 483 752

E8: Geissberger A.E. and Galeener F.L., "Raman studies of vitreous SiO_2 versus fictive temperature"; Physical Review B, vol. 28, 6, 15 September 1983

The opposition division held that the requirements of Article 100(b) EPC were met, but that the glass according to claim 1 as granted lacked novelty over a glass sample disclosed in table V of E8. The method according to claim 17 as granted (identical with claim 1 of the second auxiliary request) was not based on an inventive step in view of E7. More particularly, it came to the following conclusions: The disclosure in the specification was sufficient to enable the skilled person to determine the "structure determination temperature" ("SDT" hereinafter) as referred to in claim 1, which was different from the fictive temperature ("T_F" hereinafter) referred to in the prior art. It was plausible that a separate calibration curve had to be established for each glass ingot having different chemical and physical characteristics. Moreover, a skilled person would be able to select an appropriate size of the samples. The ppm value referred to in the claims was unclear and could be interpreted as referring to mass or mole ppm when considering novelty and inventive step.

IV. During the appeal proceedings the appellant (patent proprietor) filed four further documents in support of its arguments:

E11: Copies from a catalogue of Heraeus concerning properties of quartz glasses for optics,

E12: Mikkelsen J.C.Jr. and Galeener, F.L., "Thermal equilibration of Raman active defects in vitreous silica"; Journal of Non-Crystalline Solids 37, 1980, pages 71 to 84, E13: the first page of an article from the Journal of Non-Crystalline Solids from 1996, and

E14: copies of pages taken from the Handbook of Chemistry and Physics, 76th edition.

V. With a telefax dated 20 October 2003, the respondent (opponent) filed experimental results labelled "Abschreckversuch" (hereinafter E15) and raised a further novelty objection based on E12.

VI. Oral proceedings took place on 20 November 2003.

VII. The written and oral submissions of the parties, as far as they are relevant for the present decision, can be summarised as follows:

VIII. The appellant did not contest that in the field of glass technology, it was not entirely unusual to express the concentrations of the glass components on a mole basis. It however argued that in view of E4, E7, E11 and certain passages in the description of the patent in suit, the skilled person would easily understand that the OH-group concentration mentioned in claim 1 represented mass ppm and not mole ppm. The method for obtaining a SDT calibration curve was described in sufficient detail in the patent description. The fictive temperature T_F mentioned in E8 and E12 was not identical with the SDT, since the SDT determination involved a quenching step differing by the speed and the quenching medium used from those disclosed in E8 and E12. The experimental results E15 could not be taken into consideration since quenching was not performed within 0.2 seconds, the equilibrium was not reached and the silica glass was different. Hence the samples of E12 having a reported T_F of less than 1200 K did not anticipate the glass according to claim 1 of the patent in suit. Concerning novelty over E8, and referring to the information comprised in E12, it argued that the 900°C sample of table V had not been relaxed to its equilibrium state before quenching. Therefore, this sample did not have a SDT value falling within the range as defined in claim 1 of the patent. Having regard to inventive step, the appellant considered E4 to be a more appropriate closest prior art than E7, since it clearly referred to glasses having an OH group concentration of more than 1000 mass ppm. In its view, even when taking E7 as the closest prior art, the claimed subject-matter was not rendered obvious by common general knowledge or by any of documents E4, E5, E8 and E12. None of these documents mentioned the SDT parameter or its determination using liquid nitrogen as quenching medium. E8 and E12 were not concerned with the preparation of glasses for a specific purpose. E4, E5 and E7 described different preparation methods and were silent about the issue of scattering loss of the glasses and the contrasts obtainable therewith in photolithographic applications. Hence they could not, even if taken in combination, suggest the claimed method in order to obtain glasses improved in this respect.

According to the respondent, neither the patent itself nor the prior art documents supported the interpretation of the unclear term "ppm" as used in the claims in the sense of "mass ppm". The SDT was a new parameter for describing the structure of a quartz glass, which, like the T_F parameter known from the prior art, was based on Raman line intensity measurements. However, the method to be used for establishing the SDT calibration curve was not disclosed in the patent in a manner sufficiently clear and complete for it to be reproduced with sufficient precision by a skilled person. It pointed out that the patent in suit generally lacked important experimental details. It did not contain an example of a calibration curve and the Raman line intensities actually measured were not reported. The size of the samples used in determining the calibration was not indicated, although it had a certain influence on the quenching speed and diffusion of OH groups from and into the sample. Referring in particular to E7, E8 and E12, the respondent doubted that there was any difference at all between the SDT as determined according to the patent in suit and the fictive temperature T_F referred to in the prior art. Concerning its experimental evidence E15, it admitted that the samples had not been quenched within 0.2 seconds and that it had not been ascertained by means of Raman measurements that the samples to be quenched had actually reached their equilibrium state. Based inter alia on E15, which it considered to follow as closely as possible the instructions given in the patent in suit, the respondent was of the opinion that a glass obtained by rapidly quenching a sample previously equilibrated at a given retention temperature in water did not differ, in terms of its relative Raman line intensity I_{D2}/I_{800}, from the one obtainable by quenching said sample within 0.2 seconds in liquid nitrogen. Hence, the subject-matter of claim 1 lacked novelty in view of those "Suprasil 1" glass samples referred to in Figures 1 to 3 of E12 having a reported T_F of less than 1200 K. Information on how to obtain such glasses could also be gathered from E8, Table V. Moreover, it argued that the claimed glass lacked novelty in view of E7, which document suggested the minimisation of the $I_{606}:I_{800}$ ratio, and hence of the SDT. In particular, this document taught an I_{606}/I_{800} ratio of less than 0.15, which range encompassed the ideal ratio of 0 corresponding to a glass without structural defects measurable at 606 cm^{-1}. Such a glass would thus in any case meet the requirement of claim 1 concerning the SDT value, i.e. SDT = 1200 K or less. Considering the two-fold overlap of the disclosure of E7 with present claim 1, i.e. in terms of the OH group concentration and the SDT, the claimed glass was not novel. Even if considered novel, the claimed glass was not inventive in view of the combined teachings of documents E7 and E8 or E12. Concerning the independent method claim 17, it also argued that careful annealing and cooling was a measure which was known to be necessary for obtaining optical glasses of acceptable quality. Starting from the method disclosed in Example 13 of E7 as closest prior art, a slow cooling to a temperature lower than the one mentioned therein was an obvious measure in order to obtain a glass with reduced strain. In this context, it referred to the similar temperature profiles described in E4 and E5.

IX. The appellant requested that the contested decision be set aside and that the patent be maintained as granted or, in the alternative, on the basis of the claims filed as first or second auxiliary requests on 12 January 2001.

The respondent requested that the appeal be dismissed.

Reasons for the Decision

1. *Sufficiency of disclosure - Construction of claims*

1.1 The feature "at least 1000 ppm"

1.1.1 The contested patent does not expressly indicate whether the minimum value of the OH group concentration is expressed on a mass or on a mole basis.

1.1.2 Figure 10 and the corresponding text of the patent refer to the use of mass flow controllers (410) in the H_2 and O_2 feed lines in connection with the preparation of the silica glass (page 11, lines 30 to 43). Although the composition of the glass obtained appears to depend on the preparation process conditions, and hence *inter alia* on the ratio of the amounts of H_2 and O_2 fed to the reactor, the corresponding OH group concentration obtained is measured in the final product. As pointed out by the respondent, the results of the IR absorption spectrometric measurements (see page 16, lines 4 to 5 of the patent in suit) can be expressed on weight or mole basis, depending on the calibration method used, which is of similar complexity in both cases. Hence, in the absence of any supporting evidence, the board cannot accept the appellant's contested allegation that it is easier to determine the OH-group concentration on the basis of the mass. Therefore, the board takes the view that a skilled reader of the contested patent would not clearly and unambiguously conclude from the reference to mass flow controllers in the reagents feed-lines that the term "ppm" as used in the claims necessarily refers to OH group concentration of the final product expressed on a mass basis.

1.1.3 Those among the cited references which mention an OH-group concentration given in ppm either explicitly refer to mass ppm or remain silent about the basis to be considered in this connection, see e.g. E4, claim 1, E7, page 15, Table 1, third row, E11, second page, column "OH content", third row, E13, footnote 2, and E5, claim 1, E8, page 3266, left-hand column, second paragraph from the bottom, and E12, the paragraph bridging pages 72 and 73. However, in the literature relating to glass technology, concentrations of components have previously also been expressed on a mole basis. This fact pointed out by the board during the oral proceedings has not been disputed by the appellant and cannot be put into question by documents E13 and E14 which refer to mass based concentrations or glasses. Therefore, the board takes the view that the common general knowledge in the field of glass compositions does not either provide a sufficient basis for accepting that the term "ppm" as used in the present claims is to be equated with the expression "mass ppm".

1.1.4 The granted claims are ambiguous, and hence unclear, in that they do not specify whether the OH group concentration is expressed in mass or mole ppm. Lack of clarity not being a ground for opposition, construction of the claims is necessary in the present case. Since both meanings (mole ppm and mass ppm) are technically valid, the board shares the view of the opposition division that the claims should be constructed as encompassing both alternatives when considering novelty or inventive step over the prior art.

1.1.5 The respondent has neither contested that products having an OH group concentration of at least 1000 ppm (expressed on a mole or on a mass basis) could be obtained nor that the numerous examples given in the patent could be carried out by the skilled person. Hence, the lack of clarity concerning the basis for the ppm indication does not, as such, imply that the skilled person was not able to carry out the invention as claimed. Therefore, the board concludes that the requirements of Article 100(b) EPC are met having regard to the feature "at least 1000 ppm".

1.2 The feature "structure determination temperature"

1.2.1 In the board's view, the evidence and arguments presented by the respondent with respect to the alleged insufficiency of the disclosure in connexion with the feature SDT do not justify a reversal of the position adopted by the opposition division for the following reasons.

1.2.2 In the passages on page 3, line 54 to page 4, line 17 and on page 15, line 56 to page 16, line 1, the patent in suit discloses how the SDT of a glass as claimed can be obtained. It is in particular pointed out that a plurality of test pieces of a silica glass are retained at a plurality of temperatures within the range of 1073 to 1700 K for a period longer than the structure relaxation temperature in air, each test piece thereby having the structure in the equilibrium state at the retention temperature. The test pieces are then quenched by introducing them into liquid nitrogen in 0.2 second, in order to fix the thermal equilibrium glass structure at the retention temperature in the cooled test pieces obtained. Thereafter, a Raman scattering measurement is carried out wherein the ratio of the line intensities at 606 and 800 cm^{-1}, i.e. the intensity ratio I_{606}/I_{800}, is determined for each test piece of the silica glass. A calibration curve is drawn up from the two variables, i.e. retention temperature (corresponding to the SDT) and I_{606}/I_{800}. The unknown SDT of a further sample of said silica glass is then determined using the calibration curve by plotting the measured I_{606}/I_{800} value of a test piece of the said glass and reading the corresponding SDT value.

1.2.3 Although the patent in suit does not disclose a specific calibration curve, it contains sufficient information as to how such a curve can be obtained. It is not explicitly indicated in the patent in suit that a calibration curve is prepared for each different glass; however, the respondent did not give any reason why the absence of an explicit indication in this respect would result in the skilled person not being able to put into practice the teaching of the patent in suit. Moreover, the patent in suit does not disclose that the same calibration curve should be used for all silica glasses whatever their method of production, composition or thermal history. As according to the patent in suit the SDT is a factor which expresses the structural stability of a silica glass, it is plausible that a new calibration curve has to be made for each silica glass having different chemical and physical characteristics. This was not contested by the respondent.

1.2.4 The respondent based its argumentation that it was impossible to establish a calibration curve in the range below 1200 K on the following passages of the patent in suit:

(i) "When the retention temperature is lower than 1200 K, the structure determination temperature cannot be lowered to 1200 K or lower in a given period, and, furthermore, annealing is insufficient and strain cannot be removed" (see page 10, lines 41 to 43).

(ii) "When the annealing completion temperature is higher than 1000 K ..., the structure determination temperature cannot be lowered to 1200 K or lower ..." (see page 10, lines 50 to 53).

The board notes that both these statements are taken from a part of the description (starting at line 36 of page 10) dealing with the claimed method for producing the silica glass and not with the method for drawing up the calibration curve.

1.2.5 Passage (i) indicates that retention temperatures of less than 1200 K are not suitable for the actual production, by means of the claimed method, of a glass having the desired properties. The expression in a "given period" used in said passage cannot be interpreted in this context as meaning that the time period is not a "limited period". In the next sentence of the patent in suit (page 10, lines 43 to 44) the retention time is said to be "preferably a period of longer than the structure relaxation time at the retention temperature, especially preferably 1 to 24 hours". From the entire passage on page 10, lines 41 to 44, the board cannot derive that the time period required for attaining the equilibrium state at a retention temperature < 1200 K would be unlimited (or infinite). According to both E8 and E12, the relaxation time for the Raman line at 606 cm^{-1} is a function of the retention temperature and the level of network terminating impurities, e.g. the OH content (see E8, page 3270, left-hand column, second paragraph, and E12 page 77, lines 11 to 13 starting from the bottom of Table 1, respectively). E12 discloses that for some glasses reaching the quasi-equilibrium state may require several hundred hours of annealing (see: page 75, last full sentence), and that with the "Suprasil 1" samples tested the lower fictive (annealing) temperature limit was 1073 K (800°C) for annealing times of one month or less (see page 76, second full sentence). This seems to be in accordance with the data presented in Table 1 on page 77 of E12 (see the data for "Suprasil 1"). According to the respondent's submission during the oral proceedings, it takes about four times the indicated "characteristic relaxation time" to come close (97%) to the equilibrium state. For example, with a retention temperature of 1073 K (800°C in Table 1 of E12), the time required for equilibration would thus be at least around $4 \times 2.7 \times 10^5$ seconds or 300 hours. Establishing a calibration curve including retention temperature values of less than 1200 K would thus require a substantial amount of time, but it would be feasible. Hence, the board cannot accept the respondent's contested allegation that it would be impossible for the skilled person to establish a calibration curve at temperatures of less than 1200 K.

1.2.6 Turning now to the passage mentioned above under (ii), it does not prove either that a calibration curve cannot be made between 1073 K and 1200 K, since the test pieces for establishing the calibration curve are not subjected to the annealing treatment described in this passage (slow cooling step from the retention temperature to the annealing completion temperature) but are quenched in liquid nitrogen after having reached the equilibrium state at the retention temperature.

1.2.7 As pointed out by the appellant, test pieces of 60 mm in diameter and 10 mm in thickness are mentioned in the contested patent, see page 12, line 32. However, these particular test pieces, after having been heated to and retained at an elevated retention temperature, are slowly cooled (annealed) at the rates specified in Table 2, see page 12, lines 33 to 37. Although the same expression ("test pieces") is used in the patent in connection with the description of the method used for obtaining the calibration curve, it cannot be directly inferred from the quoted passages on page 12 that test pieces having the same dimensions were used in connection with the said calibration method. Therefore, the patent in suit does not disclose any exact shape and size of the test pieces to be used for drawing up the calibration curve.

1.2.8 However, the contested patent clearly presents the skilled person with the information that in order to fix or freeze the structure of the glass test pieces for calibration at the retention temperature, a very fast quenching is required, see page 4, lines 3 to 9. The appellant has acknowledged that the quenching rate is dependent on the type and temperature of the quenching medium, as well as on the shape and size of the test piece. The respondent has not, however, contested the finding of the opposition division according to which the skilled person, presented with the information contained in the contested patent, would realise that suitable test pieces need to be of a size sufficient to perform the Raman analysis, but not too large so as to permit the necessary instant cooling in the liquid nitrogen. This view is supported by e.g. document E12, which mentions that a sample of 3 x 4 x 8 mm^3, i.e. of a much smaller size than the "test pieces" referred to on page 12, lines 32 to 33 of the patent in suit, is suitable for Raman measurements and can be quenched rapidly, see page 73, lines 1 to 7. As pointed out by the respondent, in E12 a possible ambient-controlled in- or out-diffusion of OH in air at the prevailing temperatures is also considered when selecting the sample size, since the OH group content has a "dramatic" influence on the relaxation speed (see page 72, lines 7 to 10). However, E12 also teaches that the equilibrium Raman line intensity at 606 cm^{-1} is independent of the OH group concentration, in contrast to other published results (see abstract, page 72, lines 7 to 10). The respondent has not demonstrated that variations of the size and/or shape of a glass sample within the limits defined above would necessarily lead to an OH group diffusion of a magnitude such as to lead to significantly varying equilibrium Raman line intensity ratios I_{606}/I_{800} and SDT-values. Therefore, the board does not accept the respondent's conclusion that due to the absence of information regarding the geometry or dimensions of the samples to be quenched, the skilled person was not in a position to establish a suitable SDT calibration curve in a reproducible manner.

1.3 It follows from the above that the subject-matter of the patent meets the requirement of sufficiency of disclosure set out in Articles 83, 100(b) EPC.

2. *Novelty*

2.1 Document E12

2.1.1 E12 is a scientific article investigating the thermal equilibration of Raman active defects in vitreous silica (see title). The authors used the relative intensity of the Raman line at 606 cm^{-1} to monitor the structural relaxation of vitreous silica upon an annealing treatment, and to determine the relaxation times and the quasi-equilibrium Raman spectra as a function of the so-called "fictive temperature T_F". T_F is defined as an elevated temperature at which prior equilibrium was achieved, and from which a "sufficiently fast" quench was made, and characterises the room-temperature meta-stable state of the vitreous SiO_2. From the experimental data gathered, the authors conclude on the one hand that the time required for equilibration decreases with increasing annealing temperature (T_F) and with increasing concentrations of network terminators such as OH groups or F, and on the other hand that the equilibrium intensity of the 606 cm^{-1} Raman line is exponentially dependent on the inverse T_F. See in particular page 71, the abstract and lines 4 to 7 of section "1. Introduction", page 72, the last paragraph of section "1. Introduction" and page 83, section "6. Conclusion".

2.1.2 The experiments describe the behaviour of several kinds of silica glass, including "Suprasil 1 (type III)" and "Suprasil W1 (type IV)" samples, which respectively contain 1200 ppm and less then 2 ppm OH groups, see the sentence bridging pages 72 and 73. It can be gathered from the sections "2. Sample preparation" and "4. Experimental" that in the course of these studies, "Suprasil 1" samples of 3 x 4 x 8 mm^3 were initially annealed to equilibrium at 1373 K (1100°C) or 1473 K (1200°C). The samples were then repeatedly annealed at a given temperature T_a, rapidly transferred from the furnace into water for quenching them (page 73, line 9), and measured, until the equilibrium value of the Raman 606 cm^{-1} line intensity for the given temperature T_a was reached. More particularly, Figure 1 of E12 discloses the Raman spectrum of a "Suprasil 1" sample having a T_F of 1073 K (800°C), i.e. of a sample annealed to equilibrium according to the described method. Figure 2 *inter alia* shows the final equilibrium value of the relative Raman 606 cm^{-1} line intensity of a "Suprasil 1" sample repeatedly annealed and quenched at 1173 K (900°C) according to the same method. Figure 3 discloses *inter alia* the equilibrium 606 cm^{-1} relative intensities of three "Suprasil 1" samples annealed at temperatures in the range between about 1175 K and about 1000 K (see inverse annealing temperature 1/T range from about 0.85 to about 1 $10^{-3}K^{-1}$). E12 thus discloses several silica glass samples having a T_F in the range < 1200 K.

2.1.3 According to the patent in suit, the quenching step used in the determination of the SDT comprises introducing the thermally equilibrated test pieces into liquid nitrogen in 0.2 seconds. It is further stated that when the test pieces are instead "introduced into water, quenching is insufficient and structural relaxation occurs in the process of cooling, and the structure at the retention temperature cannot be fixed". Moreover, "adverse effect may occur due to the reaction between water and the silica glass". These drawbacks are avoided by quenching in liquid nitrogen according to the invention. See page 3, line 58 to page 4, line 9 of the contested patent. The board considers it plausible that due to the very rapid transfer and the faster quenching rate obtainable by using inert liquid nitrogen rather than water as the quenching medium, the structure of the test piece will be less affected in the course of the quenching step. Since the "frozen" structure will be closer to the structure of the equilibrium glass structure at the retention temperature applied, the measured Raman spectrum and, hence the SDT derived therefrom, will differ from the Raman spectrum obtained upon water quenching of the test piece. The SDT will thus coincide more closely with the retention temperature.

2.1.4 E12 is silent about the SDT of the glass samples and the time taken for the introduction of the sample into the quenching water. E12 merely mentions a "sufficiently fast quench" and a "rapid removal of the samples from the furnace for quenching into water", see page 71, line 6 of Section "1. Introduction" and page 73, line 9. Moreover, each sample is repeatedly quenched in the course of the experiments and hence even more prone to react with the water.

2.1.5 Relying on its experimental report E15, the respondent alleged that the samples annealed to equilibrium and quenched according to the method disclosed in E12 would inherently have the same SDT values as samples quenched according to the method of the patent in suit.

According to the said report, quenching tests were carried out with "Suprasil" glass samples of unknown origin and thermal history, having an OH group content of 1000 wt. ppm and a size of 7 x 7 x 12 mm^3. In each test, three of the samples were heated to an elevated temperature of either 1193 K (920°C) or 1373 K (1100°C), retained at that temperature for 24 hours, and then quenched in either water or liquid nitrogen. After quenching, the intensity of the 604 cm^{-1} D_2 Raman line was measured and normalised with the intensity of the 800 cm^{-1} line intensity. The reported average values of the ratio I_{D2}/I_{800} are supposed to show that there are no systematic or significant differences which could be attributed to the different quenching methods.

The board notes that the samples tested differ from the ones used according to E12. The latter are smaller in all three dimensions (3 x 4 x 8 mm^3) and have a different OH group concentration (1000 ppm), irrespective of whether a mole or mass basis is assumed. It is further not clear whether the contents of metallic impurities and other elements are identical to those of "Suprasil 1 (type III)" used in E12. Only one of the retention temperatures applied lies in the range relevant for the invention as claimed (SDT

≤ 1200 K). At the oral proceedings, the respondent moreover conceded that it had carried out the quenching rapidly, but not within 0.2 seconds as in the patent in suit, and that it had only assumed, but not ascertained by Raman measurements, that the samples had actually reached their equilibrium state.

Considering

(i) that the size of the sample may have an impact on the speed of the quenching (see point 1.2.8 above),

(ii) that the rapidity of the entire quenching step (including the speed of the transfer to the quenching medium) may have an influence on the results obtained (see point 1.2.8 above, E12, page 73, lines 3 to 15; page 76, lines 1 to 3; page 79, lines 5 to 7; page 80, last line to page 81, line 3; and E8, page 3266, right-hand column, lines 1 to 6);

(iii) that a silica glass at lower temperature (due to radiative cooling during slower sample transfer to quench medium) and/or with a different composition may have a different reactivity with water;

(iv) that according to E12 each same sample was repeatedly quenched in water; and

(v) that it has not been shown that the preparation and thermal history of the samples used, their composition and the annealing time applied (24 hours) was such as to ascertain that the samples tested had actually reached their equilibrium state before the quenching (see point 1.2.5 above as well as E8 and E12 concerning the influence of these factors on the relaxation rate and duration),

the board cannot exclude that the I_{D2}/I_{800} ratios of those specific samples of E12 which were annealed to their equilibrium state at temperatures $T_F < 1200$ K would differ from the intensity ratios of samples annealed at the same temperature but quenched in liquid nitrogen within 0.2 seconds.

2.1.6 Concerning point (iii) above, the respondent's allegation that, contrary to what is stated in the patent, the silica glass samples would not, at the retention temperatures, react with the quenching water in a way affecting the glass structure as determined by measurement of the relative 606 cm-1 line intensity, cannot be accepted in the absence of any further supporting evidence. The reference to the absence of visible devitrification on the surface of the samples and to the absence of evidence of inhomogeneous strain under crossed polarizer examination on page 73, lines 17 to 20, of E12 is not sufficient to exclude structural changes affecting the Raman 606 cm^{-1} line intensity.

2.1.7 The respondent has also pointed out that according to the patent in suit, structural relaxation would occur in the process of cooling when water was used for quenching, see: page 4, lines 3 to 5. Referring to the retention (fictive) temperatures of less than 1200 K disclosed in Figure 3 of E12, it concluded that the SDT of a sample equilibrated at a given retention temperature and then quenched in water would always be lower than the SDT of the same sample when quenched in liquid nitrogen, since the Raman 606 cm^{-1} line intensity would necessarily decrease upon such further relaxation during cooling, but that the SDT determined by quenching in liquid nitrogen would in any case be lower than the said retention temperatures, i.e. lower than 1200 K. However, the board observed that according to E12, the relationship between the equilibrium line intensities and the corresponding retention temperatures was measured on samples repeatedly quenched in water. Under these circumstances, the occurrence of relevant structural modifications, due to a repeated reaction of the hot samples with water and having a non-negligible impact on the measured relative I_{606} intensity, cannot be excluded. Therefore, the board is not convinced that the samples disclosed in E12 would necessarily have a SDT value, expressed in K and established according to the method of the present patent, of less than the indicated fictive (retention) temperatures.

2.1.8 From the above, the board concludes that even taking into consideration the experimental evidence E15 it cannot be clearly and unambiguously gathered from E12 that the specific "Suprasil 1" samples disclosed therein having a "fictive temperature" T_F of from 1073 K to 1173 K would inherently and necessarily have an SDT of 1200 K or less, when assessed by means of a calibration curve for the same glass drawn up in accordance with the contested patent.

2.1.9 The board therefore concludes that the subject-matter of claim 1 is novel over the disclosure of E12.

2.2 Document E8 is a further scientific article referring to E12 and also concerning Raman studies of vitreous silica. More particularly, it relates to studies of the first-order Raman spectra of vitreous SiO_2 as a function of the sample fictive temperature T_F for T_F values from 900°C to 1550°C (see page 3266, abstract). According to E8 the equilibrium or steady-state intensities of the defect-lines D_1 and D_2, which are assigned to the four- and threefold ring defects, increase with increasing T_F, whereas the relaxation times decrease with increasing retention temperature and OH group content (see page 3267, left-hand column, 1st paragraph and page 3270, left-hand column, 2nd paragraph). Different types of vitreous silica were investigated. Only a few measurements were carried out on "Suprasil 1" samples having an OH group content of ≈ 1200 ppm and a size of $1 \times 5 \times 10$ mm^3. Generally, in order to achieve a desired T_F, the samples were heated at $T = T_F$, and quenched by rapidly plunging them into water. To insure that the SiO_2 network had reached equilibrium at a given T_F, series of Raman spectra were taken as a function of the retention time at the retention temperature, until the measured intensities remained constant. As far as "Suprasil 1" samples are concerned, Table V of E8 reports the "characteristic relaxation time" τ_2 at an annealing temperature of 1173 K (900°C) for the Raman line intensity at around 606 cm^{-1}, which corresponds to the D_2 defect. Moreover, the parties agreed during the oral proceedings that the retention time t^* of 5.4×10^3 seconds indicated in Table V was not sufficient to reach the equilibrium state of the sample. Hence, a sample having a T_F of 1173 K (900°C) is not directly and unambiguously derivable from E8. Even accepting for the sake of argument that Table V of E8 could give sufficient information to enable the skilled person to obtain such a sample, the preceding considerations concerning E12 apply analogously to E8 (see points 2.1.4 to 2.1.8).

2.2.1 Hence, it cannot be clearly and unambiguously gathered from Table V of E8, even in view of the experimental evidence E15, that E8 discloses "Suprasil 1" samples having a SDT of 1200 K or less.

2.2.2 The board therefore concludes that the subject-matter of claim 1 is also novel over the disclosure of E8.

2.3 E7 discloses the preparation of optical members or blanks thereof for use with high-energy radiations, such as a KrF laser or an ArF excimer laser, by thermally treating and slowly cooling a lump of high-purity transparent synthetic silica glass in a high-pressure atmosphere. The glass preferably has an OH group concentration of at least 10 mass ppm, more preferably of > 50 ppm, and most preferably of > 100 ppm. E7 further teaches that the Raman line intensity ratio R_2, i.e. I_{606}/I_{800}, of the products obtained is preferably smaller than 0.15. See claims 1, 3, 5, 11, 13, 18, 19 and 24, page 4, lines 5 to 20, page 5, lines 9 to 19, page 7, lines 13 to 15. Examples 3 to 13 describe the heat treatment and cooling of samples obtained by cutting and grinding ingots of the starting glass having an OH-group concentration of 730 mass ppm to a size of 100 mm diameter x 100 mm thickness. More particularly, according to Example 13, such a sample is heated to a temperature of 1273 K (1000°C), held at this temperature for 3 hours, cooled to 1073 K (800°C) at the slow rate of 10°C/h, left to cool to 773 K (500°C) under pressure and finally "left to cool" to room temperatures at unspecified rates under a controlled depressurisation regime. The glass obtained showed a ratio R_2 of 0.14, and had an excellent durability against KrF and ArF laser irradiation. See page 8, lines 46 to 51, pages 10 to 12, Example 13, and Table 1 on pages 14 and 15.

2.3.1 Concerning the cooling regime disclosed by Example 13, the board notes that it differs from the one of claim 17 of the contested patent in that the sample is cooled at the slow cooling rate to 1073 K instead of to 1000 K or lower. Although according to E7 the sample is cooled surrounded by a pressurised atmosphere, and hence within some kind of vessel, the board is not convinced that this implicitly and necessarily means that the cooling from 1073 K to lower temperatures would necessarily occur at a cooling rate as small as 50 K/h or less as required by claim 17 with any kind of apparatus. Hence, in the absence of any further evidence, this contested allegation of the respondent cannot be accepted. Considerations whether a skilled person trying to put E7 into practice would opt for such a prolonged cooling are not relevant having regard to the examination of novelty.

2.3.2 As agreed during the oral proceedings, the OH group concentration of 730 ppm referred to *inter alia* in Example 13 corresponds roughly to a concentration of more than 2500 expressed in mole ppm, assuming a glass composition containing only SiO_2 and OH groups, and thus no impurities, which value falls within the open range indicated in claim 1.

2.3.3 It is accepted that the values of R_2 and of the SDT are both based on the measurement of the 606 cm^{-1} and 800 cm^{-1} Raman line intensities. However, E7 is silent about the SDT of the glass obtained or any method for determining it. The respondent has provided no evidence that the reported R_2 values (minimum value 0.10) of less than 0.15 of the glasses obtainable according to the examples of E7 would necessarily correspond to SDT values of 1200 K or lower. Neither did it provide evidence that the process used in Example 13 of E7, which is different from the one claimed by the patent in suit in terms of the end temperature of the controlled slow cooling, would inevitably lead to a glass having an SDT of less than 1200 K.

2.3.4 The respondent's arguments that the glass of claim 1 lacked novelty over E7 because R_2 was a measurement of structural imperfections like the SDT and the range $R_2 < 0.15$ encompassed the value $R_2 = 0$ corresponding to an ideal structure with no imperfections at all and thus necessarily lying within the claimed range of SDT, are not convincing for the following reasons: the fact that the range of $R_2 < 0.15$ encompasses the value zero does not in the present case mean that this value is disclosed, furthermore the lowest R_2 value actually achieved in the examples of E7 is 0.10 (see Table 1, Example 3), and E7 neither expressly mentions lower values nor discloses how such an ideal silica glass without any "D2 defects" associated with the Raman line 606 cm^{-1} could be produced at all. Therefore the range

$R_2 < 0.15$ does not destroy the novelty of the claimed glass.

2.3.5 The board therefore concludes that the glass of claim 1 and the method of claim 17 are also novel over the disclosure of E7.

2.4 The claimed glass and the claimed method are also novel with respect to the other documents cited by the respondent. This was not in dispute so that further considerations are not necessary. Independent claims 11 and 13, which are directed to an optical member comprising the silica glass according to claim 1 and an exposure apparatus comprising such an optical member, respectively, refer to the glass of claim 1. Therefore, they also meet the novelty requirement.

3. *Inventive step*

3.1 The respondent considered that E7 represents the closest prior art, and in particular Example 13 thereof. The board can accept this approach since this document relates to the production of high-purity silica glass preferably containing OH groups at concentrations of up to 730 mass ppm, and being suitable for use as optical member in various apparatuses employing high power laser beams such as KrF and ArF excimer lasers. E7 mentions the use of such laser beams for lithographic applications (see page 2, lines 5 to 15). The said glass has an absolute refractive index n_d of at least 1.460, a hydrogen content of at least 5×10^{16} molecules/cm^3 and an intensity ratio R_2 of < 0.17, preferably < 0.15. The method for the preparation of the said glass comprises heating the starting glass to an elevated temperature in a pressurised atmosphere, followed by controlled slow cooling at least to a temperature of 1173 K (900°C), the lowest end temperature expressly disclosed for the slow cooling step being 1073 K (800°C). The optical members produced from this glass are durable against high-power laser irradiation for a long period of time (see claims 1, 5, 11, 13, 18, 19 and 24; page 3, lines 25 to 35; page 3, line 53 to page 4, line 4; page 4, lines 17 to 20; page 5, lines 9 to 19 and lines 26 to 38, and Table 1).

3.2 Starting from this prior art, the technical problem to be solved by the patent in suit can be seen in providing a silica glass suitable for photolithographic uses which can realise a sufficiently fine and vivid image with a good contrast at wavelengths as short as 400 nm or less (see page 3, lines 23 to 25 and page 4, line 53 to page 5, line 3).

3.3 The patent proposes to solve this problem by the silica glass as defined in claim 1 which has both a high OH group concentration of at least 1000 ppm and a SDT of 1200 K or lower. The examples and comparative examples of the patent in suit show that a silica glass having a OH group concentration or a SDT lying inside the claimed ranges exhibit improved properties (relatively low scattering loss) compared to a silica glass whose SDT and/or OH group concentration are outside the claimed ranges (see Table 3 on page 15). As pointed out by the respondent, the scattering loss value achieved in Example 7 is excellent although the SDT lies above the claimed limit of 1200 K (see Table 3). However, this example is not labelled as "comparative". It differs from all other examples in terms of the "annealing rate" and the "OH group concentration" (see Tables 2 and 3). Therefore, the plausibility of the reported results cannot be assessed in a simple manner. In view of the consistency and plausibility of the data reported for the remaining thirteen examples and ten comparative examples, the board is nevertheless convinced that the stated technical problem is actually solved by the invention as claimed.

3.4 Document E7 itself deals with the problem of the degradation of the optical transmission arising when silica glasses are irradiated with high-power laser beams for a long period of time. According to E7, when the silica glass has not reached the equilibrium state during its fabrication, an unstable structure is produced, which can be detected by measuring the Raman line intensity ratio R_2. This unstable structure is believed to contribute to the decrease in optical transmission upon laser irradiation, i.e. to the poor durability of the optical member. By increasing the absolute refractive index to a level of at least 1.460 the R_2 value can be reduced to $R_2 < 0.17$, preferably $R_2 < 0.15$ (see page 2, lines 51 to 55, page 3, line 25 to page 4, line 20, page 6, lines 45 to 48).

3.4.1 It can be inferred from E7 that a glass showing a lower intensity ratio R_2 will have a better durability against laser irradiation and that the lower intensity ratio can be achieved by increasing the absolute refractive index to a value of ≥ 1.460 at 589 nm by means of the methods disclosed therein. Moreover, it can be gathered from E7 that OH groups contained in the glass also contribute to the relaxation of the glass structure by relieving strains of interatomic distances and distorted angles between the atoms in the structure, thereby improving the durability of the glass (see page 5, lines 9 to 14).

3.4.2 In connection with the production methods described in E7, and the silica glasses disclosed in its examples, the board notes the following: only two of the several examples carried out with glasses having high OH group concentrations (i.e. 600 to 730 ppm) mention a retention temperature (starting temperature of cooling step) falling in the range of 1200 to 1350 K specified in claim 17 of the patent in suit, namely Examples 6 and 13, and a retention temperature of 1273 K (1000°C) is considered to represent the minimum required for achieving satisfactory glasses (see page 6, lines 52 to 54 and page 11, lines 51 to 52). E7 also suggests a cooling rate of less than 100°C/h down to temperatures of 1173 K (900°C) to achieve the "lowest residual strain" or birefringence (see page 7, lines 13 to 15). The lowest end-temperature of the controlled, slow cooling step mentioned in the examples of E7, and in particular in Examples 6 and 13, is 1073 K (800°C), which value lies above the maximum controlled cooling end temperature according to method claim 17 of the contested patent. Moreover, Figure 1b of E7 appears to indicate, in contrast to the respondent's allegations, that a sample slowly cooled to 800°C according to the experimental conditions described, cools much faster, even in a pressurised atmosphere, when simply "left to cool". Among the said two examples, the only one leading to glasses rated excellent in terms of the desired durability is Example 13. The durability is achieved despite the less severe ("poor") conditions in terms of temperature and pressure applied by adding extra hydrogen to the pressurised atmosphere (see page 12, lines 27 to 31). The glass obtained according to Example 13 of E7, which is considered to fully meet the durability requirements, is thus obtained by a process differing from the one according to the contested patent, and it has not been shown that the R_2-value of the glass corresponded to a SDT value meeting the requirement of claims 1 and 17 of the contested patent. Moreover, E7 contains no information which could point towards the SDT parameter or a method for establishing it.

3.4.3 E7 does not address the problem of insufficient image quality with poor contrast in photolithographic applications and is silent about factors negatively affecting the quality of the image and the contrast. Hence, without applying *ex-post facto* analysis, E7 does not suggest modifying the methods disclosed therein in order to obtain a silica glass as defined in claim 1 of the patent in suit.

3.5 E8 and E12 are both scientific articles published respectively 8 and 11 years before the filing date of E7. They both investigate the relationship between the sample fictive temperatures of specific silica glasses, their OH group contents, the measured Raman 606cm^{-1} line intensities and the relaxation times and rates achieved under certain annealing conditions. None of the two documents discloses the use of silica glasses with specific properties for specific applications, let alone in connection with the production of optical members for photolithographic purposes. They also do not address any technical problems that may occur when optical members made from high purity silica glass are subjected to UV laser irradiation. For these reasons, the board does not consider either of E8 or E12 as representing the closest prior art. The respondent's arguments that the skilled person would have combined the teachings of E7 and E8 or E12, and would thus have arrived without inventive skill at a glass falling within the definition of claim 1 are not convincing for the following reasons.

3.5.1 E12 and E8 neither address the problem mentioned in E7 of improving the durability of silica glasses by increasing its resistance to UV laser irradiation, nor the problem of scattering loss and unsatisfactory contrast in photolithographic applications.

3.5.2 Both E12 and E8 show that the intensities of the Raman line at 606 cm^{-1} decrease with decreasing fictive temperature, independently of the OH group content of the silica glass. However, neither E12 nor E8 explicitly recommend lowering the fictive temperature of a glass, and hence the intensity of the D_2 Raman line, in order to obtain a glass presenting advantages in a particular field of application. Although E7 recommends R_2 values of ≤ 0.15, neither E7 nor E8/E12 contain information actually suggesting that by decreasing the end temperature of the slow controlled cooling to values lower than 1073 K (the lowest limit disclosed in E7) the scattering loss of the glass could be reduced and the contrast obtainable in photolithographic applications could be improved.

3.5.3 Moreover, the experimental method described in E8 and E12 for studying the relationship between the T_F of the glass and the intensity of the D_2 Raman line intensity, namely the annealing of the glass at T_F until the equilibrium state is reached and the subsequent rapid quenching to low temperatures in water, is very different from the process described in Example 13 of E7 for obtaining a glass suitable as an optical member for use with high-power laser beams and which has to fulfil severe optical requirements. The latter process includes in particular a very slow and careful cooling step while maintaining the glass under high pressure, which is totally in contradiction with the rapid quenching in water to room temperature disclosed in E12 and E8.

3.5.4 Hence the board concludes that, excluding *ex-post facto* considerations, the skilled person had no obvious reason to combine E7 and E8/E12.

3.6 According to a further line of argument of the respondent the method claim 17, implicitly leading to a glass as defined in claim 1 of the patent in suit, was obvious in view of E7 and common general knowledge concerning the slow and careful annealing required in the field of optical member production, as illustrated by e.g. E5.

3.6.1 In this respect, the respondent has pointed out that according to the contested patent, strain cannot be sufficiently removed when the annealing completion temperature is above 1000 K (see page 10, lines 51 to 53). It argued that in view of the disclosure of e.g. E5 the skilled person, trying to further reduce residual strain in the glasses obtained according to Example 13 of E7, would consider the slow cooling of the glass down to lower temperatures as an obvious measure inevitably leading to the method of claim 17 of the patent in suit. It was not disputed that, generally speaking, annealing with slow cooling rates was necessary to obtain a high quality optical member. However, it is expressly stated in E7 that for the glasses prepared under the specific conditions described therein, i.e. including those glasses having a relatively high OH group concentration, the "lowest residual strain" (birefringence) of less then 5 nm/cm can be achieved at cooling rates of up to 100 K/hr in the temperature range from 1200°C to 900°C, i.e. with a controlled cooling end temperatures of 1173 K (900°C) (see page 7, lines 11 to 15), said end temperature being even lower in Example 13. Thus E7 itself considers that controlled cooling to even lower end temperatures would not have any desirable effect and does not, therefore, suggest such a measure.

3.6.2 Document E5 discloses optical members for lithographic applications made of high-purity synthetic silica glass having an OH group-content of from 10 to 100 ppm, a hydrogen molecule content of ≤ 1x10 16 molecules/cm^3, a chlorine content of ≤ 200 ppm, a uniform refractive index distribution and a birefringence of not more than 5 nm/cm in order to avoid the reduction of the ultraviolet transmission upon irradiation with ultraviolet rays from e.g. excimer lasers. According to E5, OH groups are considered as impurities, and concentrations thereof above 100 ppm are found to be detrimental to the desired resistance to transmission reduction. The final annealing step of the process for obtaining said optical members comprises the heating of the moulded silica glass to a temperature of at least 1373 K (1100°C), which is higher than the maximum retention temperature indicated in claim 17 of the contested patent (see also contested patent page 10, lines 39 to 41), and a subsequent controlled slow cooling to reduce the strain (birefringence)to values of less than 5 nm/cm. Examples 1 to 5 of E5 mention cooling at rates of 30 K/hr (0.5°C/min) K or less down to end temperatures of 873 K (600°C). See in particular claim 1, Examples 1 to 5, column 3, lines 21 to column 4, line 47, column 8, lines 26 to 44 and column 16, line 57 to column 17, line 4. The argument of the respondent, according to which, at the very slow cooling rate applied, the annealing process described in E5 could be considered to encompass "maintaining" the glass at a temperature below 1373 K (1100°C) for a certain time, i.e. at any temperature in the range indicated in claim 17 of the patent in suit, is not accepted. From the wording of claim 17, it is clear that in contrast to the method of E5, the glass is first **heated to** a temperature of **at most** 1350 K, maintained at **said** temperature some time, and then cooled.

3.6.3 E5 thus expressly prescribes the use of very low OH concentrations below 100 ppm and thus teaches exactly the opposite of E7, according to which relatively high OH group concentrations are preferred for achieving a long duration of the optical members. Concerning the annealing of the glass, E5 also teaches retention temperatures higher than the 1273 K applied in Example 13 of E7 and the maximum temperature specified by claim 17 of the patent in suit. The residual strain values (less than 5 nm/cm) to be achieved according to E5 are not lower than the one reached according to E7. Moreover, E5 is silent about the issue of scattering loss and the contrast obtainable with the optical members obtained. It is also silent about the R_2 Raman line intensity ratio or the SDT values of the optical members obtained or a method for determining the latter. However, the comparison of Example 5 with comparative Example 3 of the patent shows that, under otherwise identical conditions, the retention temperature level at which the controlled cooling step begins may have an impact on the SDT of the final glass obtained. Therefore, even assuming for the sake of argument that despite the differences in terms of the OH-group concentrations and the retention temperatures used the skilled person starting from E7 would consider E5 at all, the board is not convinced that E5 suggests those modifications of the teaching of E7 which would be necessary to arrive at the method (and thus also to the product) claimed in the contested patent in a obvious manner.

3.7 Document E4 also deals with the problem of improving the resistance of silica glass optical members to optical deterioration upon exposure to a high-power ultraviolet laser beam. The solution disclosed in E4 involves making a high-purity silica glass optical member which contains OH groups in an amount of at least 50 wt. ppm, preferably of at least 100 wt. ppm, and up to 1200 wt. ppm according to one example, and which is doped with hydrogen sufficient to inhibit decreases in light transmittance due to exposure to said ultraviolet light (see page 4, lines 43 to 46; page 5, lines 6 to 11; claims 1, 2 and 26, Example 8). This document is also silent about the problem of scattering loss and insufficient contrast and the SDT parameter or methods for establishing it. Moreover, the final annealing/cooling temperature profiles specifically described in connection with the treatment of glasses with high OH group contents and of glasses with lower OH contents are different from the one specified in claim 17 of the contested patent (see page 11, lines 1 to 8, and page 17, lines 16 to 29, page 20, lines 14 to 30, respectively). Hence E4 cannot be considered to comprise further information pointing to the claimed subject-matter.

3.8 The remaining documents cited by the parties are less relevant and contain no additional information which, in combination with the preceding documents, could render the subject-matter of claim 1 or claim 17 obvious.

4. Since the subject-matter of claims 1 and 17 is not obvious, the same is true for the independent claims 11 and 13 which refer to the glass of claim 1, as well as for the dependent claims 2 to 10, 12, 14 to 16 and 18 to 21.

5. In view of the above conclusions, there is no need to further consider the appellant's auxiliary requests.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The patent is maintained as granted.

The Registrar:

A. Wallrodt

The Chairman:

M. Eberhard

M. Eberhard