



(51) International Patent Classification:  
G01N 21/958 (2006.01)

(21) International Application Number:  
PCT/US2016/035449

(22) International Filing Date:  
2 June 2016 (02.06.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
62/170,919 4 June 2015 (04.06.2015) US

(71) Applicant: CORNING INCORPORATED [US/US]; 1  
Riverfront Plaza, Corning, New York 14831 (US).

(72) Inventors: ROUSSEV, Rostislav Vatchev; 6 Fox Lane  
West, Painted Post, New York 14870 (US).  
SCHNEIDER, Vitor Marino; 6 Timber Lane, Painted  
Post, New York 14870 (US).

(74) Agent: SCHAEBERLE, Timothy M; Corning Incorporated,  
Intellectual Property Department, SP-Ti-03-01, Corning,  
New York 14831 (US).

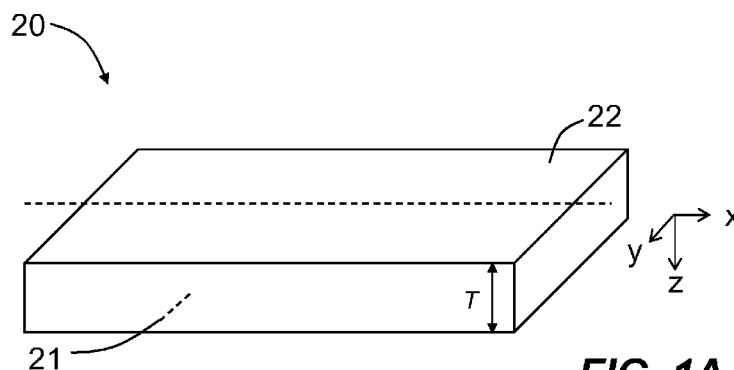
(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,  
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,  
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,  
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,  
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,  
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,  
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,  
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,  
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,  
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,  
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,  
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,  
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHODS OF CHARACTERIZING ION-EXCHANGED CHEMICALLY STRENGTHENED GLASSES CONTAINING LITHIUM



**FIG. 1A**

(57) Abstract: Methods of characterizing ion-exchanged chemically strengthened Li-containing glasses include: a) measuring a mode spectrum of the glass sample; b) using the mode spectrum, estimating a first contribution to the center tension associated with a spike region and estimating a second contribution to the center tension due to a deep region only, wherein the deep region is assumed to follow a power-law stress profile; and c) determining a total center tension by adding of the first and second contributions to the center tension. The methods can be used for quality control during manufacturing of glass samples by comparing the total center tension to a center tension specification that provides optimum strength and durability.



## **METHODS OF CHARACTERIZING ION-EXCHANGED CHEMICALLY STRENGTHENED GLASSES CONTAINING LITHIUM**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This Application claims the benefit of priority under 35 USC § 119(e) of U.S. Provisional Patent Application No. 62/170,919, filed on June 04, 2015, and which is incorporated by reference herein.

### **FIELD**

[0002] The present disclosure relates to chemically strengthened glass, and in particular relates to methods of characterizing ion-exchanged chemically glasses containing lithium.

### **BACKGROUND**

[0003] Chemically strengthened glasses are glasses that have undergone a chemical modification to improve at least one strength-related characteristic, such as hardness, resistance to fracture, etc. Chemically strengthened glasses have found particular use as cover glasses for display-based electronic devices, especially hand-held devices such as smart phones and tablets.

[0004] In one method, the chemical strengthening is achieved by an ion-exchange process whereby ions in the glass matrix are replaced by externally introduced ions, e.g., from a molten bath. The strengthening generally occurs when the replacement ions are larger than the native ions (e.g., Na<sup>+</sup> ions replaced by K<sup>+</sup> ions). The ion-exchange process gives rise to a refractive index profile that extends from the glass surface into the glass matrix. The refractive index profile has a depth-of-layer or DOL that defines a size, thickness or “deepness” of the ion-diffusion layer as measured relative to the glass surface. The refractive index profile also defines a number of stress-related characteristics, including stress profile, surface stress, center tension, birefringence, etc. The refractive index profile defines an optical waveguide when the profile meets certain criteria.

[0005] Recently, chemically strengthened glasses with a very large DOL (and more particularly, a large depth of compression) have been shown to have superior resistance to fracture upon face drop on a hard rough surface. Glasses that contain lithium (“Li-containing glasses”) can allow for fast ion exchange (e.g., Li<sup>+</sup> exchange with Na<sup>+</sup> or K<sup>+</sup>) to obtain a large DOL. Substantially power law (e.g., substantially parabolic) stress profiles are easily

obtained in Li-containing glasses, where the ion-exchange concentration profile of Na<sup>+</sup> connects in the central plane of the substrate, shrinking the traditional central zone of the depth-invariant center tension to zero or negligible thickness. The associated stress profiles have a predictable and large depth of compression, e.g., on the order of 20% of the sample thickness, and this depth of compression is quite robust with respect to variations in the fabrication conditions.

[0006] An example power law stress profile of particular commercial importance is a near-parabolic (substantially parabolic) profile for the deep region that joins to a “spike” portion near the surface. This spike portion (“spike”) is particularly helpful in preventing fracture when glass is subjected to force on its edge (e.g., a dropped smart phone) or when the glass experiences significant bending. The spike can be achieved in Li-containing glasses by ion exchange in a bath containing KNO<sub>3</sub>. It is often preferred that the spike be obtained in a bath having a mixture of KNO<sub>3</sub> and NaNO<sub>3</sub> so that Na<sup>+</sup> ions are also exchanged. The Na<sup>+</sup> ions diffuse faster than K<sup>+</sup> ions and thus diffuse at least an order of magnitude deeper than the K<sup>+</sup> ions. Consequently, the deeper portion (region) of the profile is formed mainly by Na<sup>+</sup> ions and the shallow portion of the profile is formed mainly by K<sup>+</sup> ions.

[0007] In order for chemically strengthened Li-containing glasses to be commercially viable as cover glasses and for other applications, their quality during manufacturing must be controlled to certain specifications. This quality control depends in large part on the ability to control the ion-exchange process during manufacturing, which requires the ability to quickly and non-destructively measure the refractive index (or stress) profiles.

[0008] Unfortunately, the quality control for glasses with spike stress profiles is wanting due to the inability to adequately characterize the profiles in a non-destructive manner. This inability has made manufacturing of chemically strengthened Li-containing glasses difficult and has slowed the adoption of chemically strengthened Li-containing glasses in the market.

## SUMMARY

[0009] An aspect of the disclosure is directed to methods of characterizing chemically strengthened Li-containing glasses having a surface stress spike, such as produced by an ion-exchange process whereby Li<sup>+</sup> is exchanged with K<sup>+</sup> and Na<sup>+</sup> ions (i.e.,  $\text{Li}^+ \rightleftharpoons \text{K}^+, \text{Na}^+$ ). The methods result in a measurement of the surface compression and the depth of the spike, and its contribution to the center tension, as well as the compression at the bottom of the spike, and the total center tension.

[0010] The method is preferably carried out to obtain a commercially important stress profile. An example of such a profile follows a power law (e.g., substantially parabolic) in most of the interior (“deep region”) of the substrate other than the spike region (“spike”) adjacent the substrate surface. The spike is generally formed by the slower diffusion (and thus shallower)  $K^+$  ions while the power-law portion is formed by the faster (and thus deeper) diffusing  $Na^+$  ions. The method allows for confirmation that the profile has reached the power-law, e.g., has a self-consistency check. The method can also include performing quality control of the glass samples being process. Such quality control is important for a commercially viable manufacturing process.

[0011] An aspect of the method involves measuring the mode lines or fringe spectrum of the  $K^+$  spike layer of the glass sample using a prism-coupling system to calculate surface stress (CS), depth of the spike (DOS), and the center tension (CT) contribution of the spike. In addition, a shift of an intensity transition corresponding to index at the depth of the bottom of the spike is measured, providing an estimate of the stress at the bottom of the spike. The depth of the spike ( $DOS_{sp}$ ) and the depth of layer (DOL) is used to verify that the rest of the profile is in the power-law regime. Then the total CT is estimated assuming that the profile is follows a power law, taking into account the CT contribution of the spike. If the profile is expected to deviate moderately from a power law, the expected deviation can be accounted for by an adjustment factor in the target CT. If necessary, the depth of compression (DOC) is also estimated, taking into account the reduction of DOC resulting from the spike, relative to the DOC of a power-law profile.

[0012] In another aspect of the method, relationship is defined between the measurement wavelength and the target properties of the  $Na^+$ -enriched deeper portion of the profile to help ensure a precise measurement of the compression at the bottom of the spike, and the most precise estimate of the CT and frangibility.

[0013] In another aspect of the method, a prism-coupling measurement of the mode spectrum is combined with a measurement of the weight gain, or measurements of the sample thickness and the sample weight, to estimate the amount of  $Na^+$  diffused in the sample.

[0014] Advantages of the methods disclosed herein include that they are non-destructive and high-throughput, and can provide a measurement of critical parameters of the stress profile with high precision. These parameters include the compressive stress CS, depth of

spike DOS, depth of layer DOL, center tension CT and frangibility status, which is based on the center tension CT.

[0015] Additional features and advantages are set forth in the Detailed Description that follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the embodiments as described in the written description and claims hereof, as well as the appended drawings. It is to be understood that both the foregoing general description and the following Detailed Description are merely exemplary, and are intended to provide an overview or framework to understand the nature and character of the claims.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0016] The accompanying drawings are included to provide a further understanding, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s), and together with the Detailed Description serve to explain principles and operation of the various embodiments. As such, the disclosure will become more fully understood from the following Detailed Description, taken in conjunction with the accompanying Figures, in which:

[0017] FIG. 1A is an elevated view of an example DIOX glass substrate in the form of a planar substrate;

[0018] FIG. 1B is a close-up cross-sectional view of the DIOX substrate of FIG. 1A as taken in the x-z plane and that illustrates the double ion-exchange process that takes place across the substrate surface and into the body of the substrate;

[0019] FIG. 1C schematically illustrates the result of the DIOX process that forms the DIOX substrate;

[0020] FIG. 2 is a representation of an example refractive index profile  $n(z)$  for the DIOX substrate illustrated in FIG. 1C;

[0021] FIG. 3 is a schematic representation of an example measured mode spectrum of a Li-containing glass formed by an ion-exchange process using a mixture of  $\text{NaNO}_3$  and  $\text{KNO}_3$ , with the mode spectrum including TM (top) and TE spectra (bottom), and also showing profile measurement parameters as explained below;

[0022] FIG. 4 is a plot of the stress (MPa) versus a normalized position coordinate  $z/T$ , showing the model stress profile (solid line) for a sample chemically strengthened Li-containing glass that has undergone a  $K^+$  and  $Na^+$  ion exchange, wherein the dashed line represents the model profile for  $Na^+$  diffusion only, noting that the model profile has ion exchange taking place at two surfaces that respectively reside at  $z/T = -0.5$  and  $+0.5$ ;

[0023] FIG. 5 is a plot of the stress (MPa) versus a normalized position coordinate  $z/T$  showing separate plots for the spike portion, the long diffused power-law portion and the spike plus power-law portion of the stress profile;

[0024] FIG. 6 is a schematic representation of a measured mode spectrum showing the TE and TM mode spectra for an example chemically strengthened Li-containing glass sample; and

[0025] FIGS. 7A and 7B are plots of the intensity  $I$  versus distance  $x'$  along the mode spectrum for the mode lines or fringes of TE and TM mode spectra, respectively, of FIG. 6.

#### DETAILED DESCRIPTION

[0026] Reference is now made in detail to various embodiments of the disclosure, examples of which are illustrated in the accompanying drawings. Whenever possible, the same or like reference numbers and symbols are used throughout the drawings to refer to the same or like parts. The drawings are not necessarily to scale, and one skilled in the art will recognize where the drawings have been simplified to illustrate the key aspects of the disclosure.

[0027] The claims as set forth below are incorporated into and constitute part of this Detailed Description.

[0028] In the discussion below, the term “power law” refers to a function that in an example follows the general form  $f(x) = ax + bx^2 + cx^3 + dx^4 \dots$ , where  $a$ ,  $b$ ,  $c$  and  $d$  are coefficients.

[0029] FIG. 1A is an elevated view an example glass substrate in the form of a planar ion-exchanged substrate 20 that has a body 21 and a (top) surface 22, wherein the body has a base (bulk) refractive index  $n_s$ , a surface refractive index  $n_0$  and a thickness  $T$  in the  $z$ -direction. FIG. 1B is a close-up cross-sectional view of ion-exchanged substrate 20 as taken in the  $y$ - $z$  plane and illustrates an example double ion-exchange (DIOX) process that takes place across surface 22 and into body 21 in the  $z$ -direction.

[0030] In the DIOX process discussed in connection the method disclosed herein, two different types of ions  $\text{Na}^+$  and  $\text{K}^+$  replace another different ion  $\text{Li}^+$  that is part of the glass body 21. The  $\text{Na}^+$  and  $\text{K}^+$  ions can be introduced into the glass body 21 either sequentially or concurrently using known ion-exchange techniques. As noted above, the  $\text{Na}^+$  ions diffuse faster than the  $\text{K}^+$  ions and thus go deeper into the glass body 21. This has an effect on the resulting refractive index profile and stress profile, as discussed below.

[0031] FIG. 1C is a schematic diagram of the resulting DIOX process, and FIG. 2 is a representation of an example refractive index profile  $n(z)$  for substrate 20 having undergone the DIOX process and having a refractive index profile such as illustrated in FIG. 1C. The corresponding stress profile can be represented by  $\sigma(z)$ . The refractive index profile  $n(z)$  includes a first “spike” region R1 associated with the shallower ion-exchange ( $\text{K}^+$  ions) and that has a depth D1 into body 21 that defines a “depth-of-layer for the spike” denoted hereinafter as  $\text{DOL}_{\text{sp}}$ . The refractive index profile  $n(z)$  also includes a second region R2 associated with the deeper ion-exchange ( $\text{Na}^+$  ions) and that has a depth D2 that defines the depth-of-layer (DOL).

[0032] The deeper second region R2 may be produced in practice prior to the shallower region. The region R1 is adjacent substrate surface 22 and is relatively steep and shallow, whereas region R2 is less steep and extends relatively deep into the substrate to the aforementioned depth D2. In an example, region R1 has a maximum refractive index  $n_0$  at substrate surface 22 and steeply tapers off to an intermediate index  $n_i$ , while region R2 tapers more gradually from the intermediate index down to the substrate (bulk) refractive index  $n_s$ . The portion of the refractive index profile  $n(z)$  for region R1 represents a “spike” in the refractive index having a depth DOS.

[0033] FIG. 3 is schematic representation of an example measured mode spectrum 50 of a Li-containing glass formed by an ion-exchange process using a mixture of  $\text{NaNO}_3$  and  $\text{KNO}_3$ , with the mode spectrum including TM and TE spectra 50TM and 50TE (upper and lower portions, respectively) with respective mode lines 52TM and 52TE. The glass type is 196HLS with a fictive temperature of 638 °C. The glass was subjected to a  $\text{Li}^+ \leftrightarrow \text{K}^+$ ,  $\text{Na}^+$  ion-exchange process by placing the glass sample in a bath having 60 wt%  $\text{KNO}_3$  and 40 wt%  $\text{NaNO}_3$  at 390 °C for 3 hours.

[0034] As is known in the art, the fringes or mode lines 52TM and 52TE in the mode spectrum can be used to calculate surface compression or “compressive stress” CS and depth

of layer DOL associated with an ion-exchange layer that forms an optical waveguide. In the present example, the mode spectrum 50 was obtained using a commercially available prism-coupling system, namely the FSM6000L surface stress meter ("FSM system"), available from Luceo Co., Ltd. of Tokyo, Japan. Example prism-coupling systems suitable for use for carrying out the methods disclosed herein are also described in U.S. Patent Applications No. 2014/0368808 and 2015/0066393, which are incorporated by reference herein.

[0035] The measured values of CS and DOL were 575 MPa and 4.5 microns, respectively. These are the parameters of the K<sup>+</sup> enriched layer or spike region R1 adjacent sample surface 22. The auxiliary vertical dashed lines on the left hand side of the spectrum were added to FIG. 3 and show positions in the spectrum in which the conventional FSM system assigns to correspond to the surface index, one for TM, and one for TE. The difference in these positions is proportional to the surface stress or compressive stress CS. These positions are also used in the calculation of DOL.

[0036] The present inventors have recognized that in the mode spectrum 50 for a chemically strengthened Li-containing glass having undergone a Li<sup>+</sup> ⇌ K<sup>+</sup>, Na<sup>+</sup> ion exchange, the position of transition from the bright to the dark portion of the spectrum, observed after the last fringe 52 in the spectrum that corresponds to the highest-order guided mode, is shifted in the TE spectrum 50TE as compared to the TM spectrum 50M. This shift is proportional to the compressive stress CS at the depth at which the K<sup>+</sup> concentration in spike region R1 decreases approximately to the constant-level concentration originally in the substrate (e.g., the spatially constant concentration in the glass matrix that makes up substrate body 21). The effective index of the transition corresponds to the effective index that occurs at the depth of a characteristic "knee" or transition in the stress profile, and the shift of the transition between the TE and TM spectra is proportional to the stress at the depth of the knee.

[0037] The measurements of the mode spectrum 50 provided by the K<sup>+</sup> penetration resulting from ion exchange, along with the shift in the intensity transition (e.g., transition from total internal reflection (TIR) to partial reflection as defined by the critical reflection angle in the prism-coupler system used), can be combined and used for effective quality control of a family of stress profiles that provide superior resistance to fracture. The profiles of this family are similar in shape to a power-law profile (region R2) with a spike (region R1). The spike is small in thickness when compared to the substrate thickness T. For example, the spike may be 10 microns deep (i.e., DOL<sub>sp</sub> = 10 microns), while the substrate

may be  $T = 800$  microns thick. The spike may have a shape similar to a complementary error function (erfc) shape, but may also be similar to a linear depth distribution, Gaussian depth distribution, or another distribution. The main features of the spike are that it is a relatively shallow distribution and it provides substantial increase of surface compression over the level of compression at the bottom of the spike as defined by  $DOL_{sp}$ .

**[0038]** FIG. 4 is a plot of the stress (MPa) versus a normalized position coordinate  $z/T$ , showing the model stress profile (solid) for a sample chemically strengthened Li-containing glass that has undergone a  $K^+$  and  $Na^+$  ion exchange, wherein the dashed line represents the model profile for  $Na^+$  diffusion only (note that the model profile has ion exchange taking place at two surfaces that respectively reside at  $z/T = -0.5$  and  $+0.5$ ). The profile has a parabolic deep portion or region R2 and a surface spike portion or region (or just “spike”) R1.

**[0039]** In the present disclosure, the assumed convention is that compressive stress CS is positive and tensile stress is negative. The model profile of FIG. 4 has a linear spike R1 added on top of a deep quadratic profile R2. Another feature of the spike is also recognized from FIG. 4, namely that the typical slope of the stress distribution in the spike R1 is significantly higher than the typical slope in the deep portion R2 of the profile, which is assumed to follow a power law, and can be approximated as parabolic for the purposes of making measurements that can be used for quality control.

**[0040]** The profiles that are adequately approximated as parabolic for the purposes of the quality-control measurement method of the present disclosure have a distribution of  $Na^+$  ions such that over the range of depths from the bottom of the spike to the center of the thickness (i.e., from  $z = DOL_{sp}$  to  $T/2$ ), the minimum  $Na^+$  concentration is at the center of the thickness (i.e., at  $x/L = 0$  in FIG. 4), and the increase in concentration at the bottom of the spike relative to the minimum concentration at the center of thickness is approximately 3 to 7 times higher than the increase in concentration at a depth equal to one quarter of the thickness, i.e.,  $T/4$ . In some cases, the increase in  $Na^+$  concentration anywhere within the depth of the spike relative to the concentration in the center of the substrate may be 3 to 7 times higher than the increase in  $Na^+$  concentration (relative to the center concentration) at depth equal to one quarter of the thickness.

**[0041]** In one embodiment of the method, the CS and DOL of the spike are measured using a conventional prism-coupling measurement, e.g., using the aforementioned FSM system. Then a CT contribution of the spike  $CT_{SP}$  is calculated using the equation:

$$CT_{sp} = \frac{CS_{sp} \times DOL_{sp}}{T - DOL_{sp}}$$

where  $T$  is the aforementioned sample thickness. The contribution to center tension of the  $Na^+$  profile  $CT_{par}$ , which is assumed parabolic, is calculated as:

$$CT_{par} \approx |0.5\sigma_{knee}|$$

where  $\sigma_{knee}$  is the stress at the knee of the profile, e.g., at the bottom of the spike and is given by:

$$\sigma_{knee} = \frac{(n_{crit}^{TE} - n_{crit}^{TM})}{SOC}$$

where  $n_{crit}^{TE}$  and  $n_{crit}^{TM}$  are the effective indices of the critical-angle intensity transitions as illustrated on figure 1. SOC is the stress-optic coefficient.

[0042] As illustrated by the dashed line of FIG. 2, the assumed power-law profile may be considered as an auxiliary profile that does not include the spike and that extends the profile shape all the way to the surface of the sample. This auxiliary profile is force-balanced, having its own CT, and is hence shifted vertically from the power-law portion of the model spiked power-law profile. The auxiliary profile has a compression depth is given by

$$DOC_{par} = 0.5T \left(1 - \frac{1}{\sqrt{3}}\right) \approx 0.2113 T$$

[0043] The total center tension equals the sum of the contributions of the spike and of the power-law portion:

$$CT_{tot} = CT_{par} + CT_{sp}$$

The depth of compression DOC of the spiked power-law profile can be calculated by using the expression:

$$DOC = 0.5T \left(1 - \sqrt{\frac{CT_{tot}}{3CT_{par}}}\right) = 0.5T \left(1 - \sqrt{\frac{1}{3} \left(1 + \frac{CT_{sp}}{CT_{par}}\right)}\right) \approx DOC_{par} \left(1 - \frac{CT_{sp}}{2CT_{par}(\sqrt{3}-1)}\right) \approx DOC_{par} - \frac{0.5T}{\sqrt{3}} \frac{CT_{sp}}{2CT_{par}}$$

The approximate expressions at the end of the above equation are valid when the CT contribution of the spike is significantly smaller than the CT contribution of the auxiliary power-law profile.

[0044] In summary, the above-described method includes: 1) measuring the mode spectrum due to the spike and estimating a contribution of the spike to the center tension; 2) using the

mode spectrum, measuring the shift of the critical angle; 3) estimating a compression at the knee, which is proportional to the contributions of the substantially power-law profile and of the spike.

[0045] In addition, a compression depth DOC of the profile may be estimated by using an exact formula for the model profile, or an approximate formula that gives the DOC as the DOC of an auxiliary power-law profile (e.g., parabolic or nearly parabolic) less a small DOC reduction due to the spike.

[0046] Furthermore, in one example embodiment, the depth of spike  $DOL_{sp}$  is used to verify that the deep portion of the profile (region R2) is in a regime well represented by the power-law profile shape. In particular, as the  $DOL_{sp}$  of the spike increases, the penetration of  $Na^+$  increases approximately in proportion to the  $DOL_{sp}$  of the spike. Hence, for a glass where simultaneous in-diffusion of  $K^+$  and  $Na^+$  is used, a minimum  $DOL_{sp}$  can be set for any particular glass thickness, above which the deep portion of the profile can be considered to follow a power law. In another example, an upper limit of the  $DOL_{sp}$  may also be imposed to exclude physical profiles that start to deviate substantially from the parabolic model as a result of stress relaxation, which may become prominent at very long ion exchange times at high temperature.

[0047] The above-described method is a somewhat simplified version of a more precise method. The simplification incurs only a minor error when the CT contribution of the spike is much smaller than the CT contribution of the auxiliary power-law profile. The CT contribution of the spike shifts the power-law portion vertically by the amount  $CT_{sp}$  relative to the auxiliary power-law profile. As a result, the compression at the knee of the model spiked profile is actually smaller than the compression of the auxiliary profile at the knee depth by the amount  $CT_{sp}$ .

[0048] Furthermore, there is a minor change in compression of the auxiliary power-law profile between the surface and the depth of the knee, and, for a force-balanced power-law profile the CT is actually equal to half of the surface compression.

[0049] The following steps represent an example of a more precise method for determining the parameters of the model spiked power-law profile from the prism-coupling measurements:

a) Calculate preliminary  $CT_{sp}^{(0)} = \frac{(CS_{tot} - CS_{knee}) \times DOL_{sp}}{T - DOL_{sp}}$

- b) Calculate preliminary  $CS_{par}^{(0)} = \frac{CS_{knee} + CT_{sp}^{(0)}}{1 - 6\frac{DOL_{sp}}{T} + 6\frac{DOL_{sp}^2}{T^2}}$
- c) (Optional alternative to steps 4,5, and 6) Calculate preliminary  $CT_{par}^{(0)} = 0.5CS_{par}^{(0)} = 0.5\frac{CS_{knee} + CT_{sp}^{(0)}}{1 - 6\frac{DOL_{sp}}{T} + 6\frac{DOL_{sp}^2}{T^2}}$  and  $CT_{tot}^{(0)} = CT_{par}^{(0)} + CT_{sp}^{(0)}$
- d) Calculate more precise  $CT_{sp}^{(1)} = \frac{(CS_{tot} - CS_{par}^{(0)}) \times DOL_{sp}}{T - DOL_{sp}}$
- e) Calculate more precise  $CS_{par}^{(1)} = \frac{CS_{knee} + CT_{sp}^{(1)}}{1 - 6\frac{DOL_{sp}}{T} + 6\frac{DOL_{sp}^2}{T^2}}$ , and  $CT_{par}^{(1)} = 0.5CS_{par}^{(1)} = 0.5\frac{CS_{knee} + CT_{sp}^{(1)}}{1 - 6\frac{DOL_{sp}}{T} + 6\frac{DOL_{sp}^2}{T^2}}$
- f) Calculate more precise  $CT_{tot}^{(1)} = CT_{par}^{(1)} + CT_{sp}^{(1)}$
- g) (Optional) – Can continue iteration, finding more and more precise values for  $CT_{sp}$  and  $CS_{par}$  until desired level of convergence or precision. More than one iteration would rarely be of use, since actual profiles are unlikely to be precisely power law and have a precisely linear spike. More than one iteration may be useful in relatively thin substrates in which the depth of the spike may represent more than about 3% of the substrate thickness.
- h) (Optional) Determine depth of compression DOC of the profile, for example using one of the forms of the equation:

$$DOC = 0.5T \left( 1 - \sqrt{\frac{CT_{tot}}{3CT_{par}}} \right) = 0.5T \left( 1 - \sqrt{\frac{1}{3} \left( 1 + \frac{CT_{sp}}{CT_{par}} \right)} \right) \approx DOC_{par} \left( 1 - \frac{CT_{sp}}{2CT_{par}(\sqrt{3}-1)} \right) \approx DOC_{par} \cdot \frac{0.5T}{\sqrt{3}} \frac{CT_{sp}}{2CT_{par}}$$

**[0050]** In the case where one is working directly with the DOL as measured by conventional means and not the real depth of layer or position of the spike, a range of approximations may be needed, some of which are empirical in nature.

**[0051]** In many cases, the power-law profile can be estimated as parabolic or substantially parabolic, i.e., to the power 2. In other cases, substantially nonlinear diffusion may cause the shape of the deep portion of the stress profile to be best represented by a relatively high power-law profile, e.g., to the power 3, i.e., cubic, or even higher. The methods that employ profiles greater than parabolic can be used to improve the accuracy with which the quality-control model represents the actual stress profile, and in this way to increase the range of ion exchange conditions over which the quality control method works effectively for the particular glass of interest.

**[0052]** For example, for a parabolic profile the ratio of CS to CT by absolute value is 2. Similarly, for a cubic profile the corresponding ratio is 3, and for a quartic profile it is 4. A force-balanced profile representation using the power of 3/2 has a CS to CT ratio of 1.8. Note that for power-function profile where the power is not an even number, the profile is constructed as the absolute value of the power function. In the mentioned examples, the

depth of compression for the non-spiked auxiliary profile is about 0.23T for the profile with power 3/2, 0.21T for the power-law profile, 0.185T for the cubic profile, and 0.165T for the quartic profile.

[0053] Once a model-profile shape is found to represent the relatively stable shape of the center-connected concentration and stress profile, the corresponding ratio of CS to CT and DOC estimate can be used for the auxiliary profile in the application of the method of the present invention for quality control.

[0054] Thus, in a more generic embodiment of the invention, the auxiliary deep portion of the spiked profile may be represented with a symmetric absolute value of a power function of the distance from the center, and an associated ratio of CS to CT of a force-balanced profile having the shape of the model function is used to estimate the CT from the measured compression at the knee or estimated compression at the surface. If the depth of compression is also sought, the depth of compression of the model profile may be used as an approximate reference, or the depth of compression of the full force-balanced model profile may be calculated as was done for the example spiked power-law profile. In an example, the ratio CS to CT ranges from about 1.8 to about 4, while the DOC for the auxiliary model profile ranges from about 0.16T to about 0.23T.

[0055] FIG. 5 is a plot of the stress (MPa) versus a normalized position coordinate  $x/L$  and shows separate plots for the spike portion, the long diffused power-law portion and the spike plus power-law portion of the stress profile. Another embodiment uses the parabolic auxiliary profile as illustrated in FIG. 4 and the following representation for the force-balanced power-law profile (the solid red line):

$$\sigma_1\left(\frac{z}{L}\right) = \sigma_1(0) \left[ -\frac{1}{2} + 6\left(\frac{z}{L} - 0.5\right)^2 \right] \quad (1)$$

[0056] A conventional measurement (e.g., using the aforementioned FSM system) is used to measure “*FSM\_DOL*” of the spike as approximately the diffusion depth given by  $2\sqrt{D\tau}$  where  $D$  is the diffusion coefficient and  $\tau$  is the time of diffusion. Then, using the fact above where  $\sim 1.25 \times \text{FSM\_DOL}$  leads to most of the area of the spike to be included, one can get an approximate equation for the CT due to the spike contribution, namely

$$CT_{\text{spike}} = \frac{(\sigma_2'(0) - \sigma_2'(1.25 \times \text{FSM\_DOL})) \times 1.25 \times \text{FSM\_DOL}}{T - 1.25 \times \text{FSM\_DOL}} \quad (2)$$

[0057] The point  $\sigma_2'(1.25 \times FSM\_DOL)$  although not equal to is acceptably close to the CS between the transition between guided modes and continuum in the spiked lithium glass samples. This point is called the  $CS_{knee}$  and is shown in FIG. 3 as a reasonable approximation. It is also reasonable to approximate the stress and the offset due to the contribution of the  $CT_{spike}$  deeper inside the glass.

[0058] Since the power-law profile will be slowly varying as compared to the spike portion of the profile, it can be assumed that the stress at  $\sim (2-3) \times FSM\_DOL$  in the power-law region would not feel the presence of the spike. It therefore follows that:

$$\sigma_1\left(\frac{Z}{L}\right) \cong \sigma_1'\left(\frac{Z}{L}\right) + CT_{spike} \quad (3)$$

and,

$$\sigma_1\left(\frac{3 \times FSM\_DOL}{L}\right) \cong \sigma_1'\left(\frac{3 \times FSM\_DOL}{L}\right) + CT_{spike} \quad (4)$$

Using the parabolic power-law equation in (1), one establish the following relationships:

$$\sigma_1\left(\frac{3 \times FSM\_DOL}{L}\right) = \sigma_1(0) \left[ -\frac{1}{2} + 6 \left( \frac{3 \times FSM\_DOL}{L} - 0.5 \right)^2 \right] \cong \sigma_1'\left(\frac{3 \times FSM\_DOL}{L}\right) + CT_{spike} \quad (5)$$

and

$$\sigma_1(0) \cong \frac{\sigma_1'\left(\frac{3 \times FSM\_DOL}{L}\right) + CT_{spike}}{\left[ -\frac{1}{2} + 6 \left( \frac{3 \times FSM\_DOL}{L} - 0.5 \right)^2 \right]} \quad (6)$$

[0059] Numerically it can be demonstrated that if one uses a factor 2 instead of 3, the results are almost the same, in some cases varying by just 1 %-2% of  $\sigma_1(0)$ . Therefore, if one can find the approximated value of  $\sigma_1'\left(\frac{3 \times FSM\_DOL}{L}\right)$  or  $\sigma_1'\left(\frac{2 \times FSM\_DOL}{L}\right)$  in the FSM, one can use equation (6) to compute the original stress of the first stress parabola within this range of error.

[0060] In practice one can measure approximately  $\sim \sigma_1'\left(\frac{3 \times FSM\_DOL}{L}\right)$  to  $\sim \sigma_1'\left(\frac{2 \times FSM\_DOL}{L}\right)$  by examining the stress generated at the transition between guided modes and continuum in the spike on Li-glass samples. This point where approximately  $\sim \sigma_1'\left(\frac{3 \times FSM\_DOL}{L}\right)$  to  $\sim \sigma_1'\left(\frac{2 \times FSM\_DOL}{L}\right)$  can be used as the point  $CS_{knee}$  as shown in FIG. 3 as a reasonable approximation that can be measured by computing the distance between these lines (fringes) in TM and TE spectra and their refractive index. In light of the stress optical coefficient (SOC) of the material the

division of the index difference at this point per the SOC would lead to the  $CS_{knee}$  stress values.

[0061] This in addition to the  $FSM\_DOL$  and the  $CS \sim \sigma_2'(0)$  given by the FSM for the spike. Therefore  $CT_{parabola} = CT_{par} \sim \sigma_1(0)/2$ , and  $CT_{spike}$  is given in (2) as (repeated for convenience)

$$CT_{spike} = \frac{(\sigma_2'(0) - \sigma_2'(1.25 \times FSM\_DOL)) \times 1.25 \times FSM\_DOL}{T - 1.25 \times FSM\_DOL} \quad (2)$$

From there, one can (repeating the previous equations) then compute the total center tension equals the sum of the contributions of the spike and of the power-law portion:

$$CT_{tot} = CT_{par} + CT_{spike} \quad (7)$$

If desired the depth of compression of the spiked power-law profile can be calculated/estimated by using the expression:

$$DOC_{total} = 0.5T \left( 1 - \sqrt{\frac{CT_{tot}}{3CT_{par}}} \right) = 0.5T \left( 1 - \sqrt{\frac{1}{3} \left( 1 + \frac{CT_{sp}}{CT_{par}} \right)} \right) \approx DOC_{par} \left( 1 - \frac{CT_{sp}}{2CT_{par}(\sqrt{3} - 1)} \right) \approx DOC_{par} \cdot \frac{0.5T}{\sqrt{3}} \frac{CT_{sp}}{2CT_{par}} \quad (2)$$

[0062] These equations assume that the deep part of the profile is approximately parabolic in nature and has an added spike near the surface. Its validity is better matched when the spike is small in stress amplitude and not so deep in comparison to the deeper power-law portion of the profile.

[0063] An aspect of the disclosure is the use the algorithm described by the above equations to process measured mode spectra. FIG. 6 is a schematic representation of a measured mode spectrum showing the TE and TM mode spectra based on actual measured mode spectra for an example chemically strengthened Li-containing glass sample. In this case using the algorithm above considering that both  $\sigma_2'(1.25 \times FSM\_DOL) \sim CS_{knee}$  and that  $\sigma_1' \left( \frac{3 \times FSM\_DOL}{L} \right) \sim CS_{knee}$  as reasonable approximations, one can find that:

$$FSM\_DOL = DOL_{sp} = 7.77 \text{ um}$$

$$\sigma_2'(0) = CS_{spike} = 482.6 \text{ MPa}$$

$$CS_{knee} = 138.8 \text{ MPa}$$

$$CT_{spike} = 4.23 \text{ MPa}$$

$$CS_{parabola} = \sigma_1'(0) = 172.3 \text{ MPa}$$

$$CT_{\text{parabola}} = 86.14 \text{ MPa}$$

$$CT_{\text{total}} = 90.4 \text{ MPa}$$

$$DOC_{\text{parabola}} = 169 \text{ um}$$

$$DOC_{\text{total}} = 163.4 \text{ um}$$

**[0064]** The method of measurement of the compression at the knee as described above has some accuracy limitations. For any particular measurement wavelength, there are certain quasi-periodic ranges of the spike DOL within which the accuracy of the measurement of the critical-angle shift is reduced. The cause of this reduction is the appearance of a leaky mode with an effective index close to that of the critical angle as the DOL is increased from a range where the critical-angle transition is clear-cut.

**[0065]** In the example of FIG. 3, the signature of such a leaky mode can be observed in the TM mode spectrum as the extra-dark relatively narrow band immediately on the right-hand-side of the transition from bright to dark. When the leaky mode has an effective index very close to the critical-angle index, the shape of the critical-angle transition is changed by the leaky mode, resulting in error in the measurement of the shift. When a leaky mode affects only the critical-angle transition for the TM spectrum, the compression at the knee is slightly over-estimated. When it affects only the critical-angle transition for the TE spectrum, the compression at the knee is slightly under-estimated. When a leaky mode affects both the TM and the TE transition, the net error of the compression at the knee could be positive or negative, and smaller as compared to the error when the transition for only one polarization is substantially affected.

**[0066]** Consequently, aspects of the measurement methods disclosed herein are directed to eliminate or mitigate the error in the measurement of the knee compression that is caused by the presence of a leaky mode. In one embodiment, the target  $DOL_{sp}$  is selected such that the effective index of a leaky mode is not close to the critical-angle transition, neither for the TM nor for the TE polarization. If such a choice of  $DOL_{sp}$  is not available within the range of preferable overall product stress-profile designs, then the measurement wavelength is chosen such that a leaky mode at the measurement wavelength is not close to the critical angle at either polarization. The way the DOL is measured traditionally is by assigning a fraction of a mode to the index range between the highest-order guided mode and the critical angle for the purposes of mode counting, to provide a continuous measured DOL as a function of increasing diffusion depth by using a continuously varying number of modes.

[0067] The equation for the DOL is:

$$DOL = \frac{(2N - 0.5)\lambda}{3.77\sqrt{n\Delta n}}$$

where  $n$  is the approximate average index of the measured waveguiding layer, and  $\Delta n$  is the difference between the maximum and minimum index of the waveguide assumed to have a truncated linear profile. In the case of the measurement of the spike,  $\Delta n$  refers to the difference between the surface index and the index at the knee of the stress profile.  $N$  is the continuous number of modes. In the example of FIG. 3,  $N$  is approximately 2.6 modes for the TM spectrum and 2.4 modes for the TE spectrum.

[0068] The condition for selecting a preferred target DOL or a preferred measurement wavelength is that the non-integer part of the number of modes  $N$  be between about 0.1 and 0.6 at both the TM and TE polarization. Hence, in one embodiment of the invention, the measurement wavelength and the depth of the spike are such that the non-integer part of the number of modes is between about 0.1 and 0.6 at both polarizations, preferably between 0.2 and 0.55.

[0069] In another less restrictive embodiment, a correction for the effect of the leaky mode is made during the interpretation of the measured shift of the critical transition. The non-integer part of each of the TM and TE number of modes is taken into account, and a correction is made that accounts effect of the leaky mode. To this end, a calibration of the effect of the leaky mode of each polarization on the measured knee compression may be used. In an example, a sequence of samples having  $DOL_{sp}$  increasing in small steps is fabricated in the same salt mixture and at the same temperature, and used for the calibration. The actual compression at the knee decreases monotonically and smoothly with increasing  $DOL_{sp}$ , while the estimated compression fluctuates above and below the smooth dependence of the actual compression on  $DOL_{sp}$  as a result of the error induced by the leaky mode. By tracking the dependence of the fluctuation on the non-integer part of the TM and TE mode numbers, the calibration of the necessary correction is obtained.

[0070] In another embodiment, the intensity profile in the vicinity of the critical angle is analyzed, the contribution of the leaky mode is estimated based on the shape of the intensity profile and the non-integer mode number, and the estimated contribution is corrected for in the intensity profile to calculate a more accurate position of the critical angle. This is done independently for the TM and the TE polarization, and the stress at the knee is estimated after the TM and TE critical angles are found following the application of the intensity corrections.

[0071] In another embodiment, the weight gain of a sample as a result of ion exchange is used in combination with the prism-coupling measurement. The weight gain may be used to verify that enough Na ions have exchanged for Li ions such that the use of the power-law profile model is valid for quality control. For the purpose, a target acceptable weight gain range is prescribed for the ion exchange based on the total surface area of the sample and the sample thickness. The weight of representative samples is measured before and after ion exchange, and the quality-control prism-coupling measurements are considered valid if the measured weight gain per sample falls in the target range.

[0072] In another embodiment of the method, advantage is taken of the precise control of the sample shape, and of individual-sample thickness measurements that are common in some production processes. In this case it is possible to verify that the sample has had adequate weight gain by simply measuring the sample thickness with high precision (such as  $\pm 2$  microns), and measuring the post-ion exchange weight of the sample. From the known shape specification, the measured thickness, and the known density of the pre-ion-exchanged glass, the weight of the pre-ion-exchanged sample is calculated. A correction factor may be applied that accounts for a typical volume change as a result of ion exchange. The weight gain then is estimated by subtracting from the measured post-ion-exchange weight the estimated pre-exchanged weight. If the weight gain falls within the target range, the profile is deemed adequately represented by the quality-control model profile, and the prism-coupling QC measurement is considered valid.

[0073] It will be apparent to those skilled in the art that various modifications to the preferred embodiments of the disclosure as described herein can be made without departing from the spirit or scope of the disclosure as defined in the appended claims. Thus, the disclosure covers the modifications and variations provided they come within the scope of the appended claims and the equivalents thereto.

What is claimed is:

1. A method of measuring a center tension in a chemically strengthened Li-containing glass sample having a surface and a body, comprising:
  - a) performing an ion-exchange process that exchanges  $\text{Li}^+$  ions in the glass sample with  $\text{Na}^+$  and  $\text{K}^+$  ions, wherein the  $\text{K}^+$  ions and  $\text{Na}^+$  ions define a stress profile that includes a spike region adjacent the sample surface and defined substantially by the  $\text{K}^+$  ions and deep region that extends from a bottom of the spike region into the glass body and defined substantially by the  $\text{Na}^+$  ions;
  - b) measuring a mode spectrum of the glass sample;
  - c) using the mode spectrum, estimating a first contribution to the center tension associated with the spike region and estimating a second contribution to the center tension due to deep region only, including approximating the stress profile of the deep region using a power-law stress profile; and
  - d) determining a total center tension by adding of the first and second contributions to the center tension.
2. The method according to claim 1, wherein the stress profile defines a critical angle at which the mode spectrum can be measured using a prism-coupling system, and further including:
  - measuring a shift in the critical angle caused by the spike region of the stress profile relative to having no spike region;
  - using the shift in the critical angle, estimating an amount of compression at a knee in the stress profile; and
  - using the estimated amount of compression at the knee in the stress profile to obtain the estimate second contribution to the center tension.
3. The method according to claim 1, further comprising performing quality control of the formation of chemically strengthened Li-containing glass samples by forming multiple chemically strengthened Li-containing glass samples according to act a) and performing acts b) through d) to non-destructively measure the center tension of the multiple glass sample and adjusting act a) so that the center tension falls within a center tension specification.

4. The method according to claim 1, wherein the power-law stress profile is approximated to be substantially parabolic.
5. A method of measuring a center tension in a chemically strengthened Li-containing glass sample having a surface and a body and that a stress profile form by an exchange of Li ions with Na<sup>+</sup> and K<sup>+</sup> ions, wherein the stress profile includes a spike region adjacent the sample surface and deep region that extends from a bottom of the spike region into the glass body, the method comprising:
  - a) measuring a mode spectrum of the glass sample;
  - b) using the mode spectrum, estimating a first contribution to the center tension associated with the spike region and estimating a second contribution to the center tension due to the deep region only, wherein the deep region is assumed to follow a power-law stress profile; and
  - c) determining a total center tension by adding of the first and second contributions to the center tension.
6. The method according to claim 5, further comprising performing quality control of the formation of chemically strengthened Li-containing glass samples by:
  - forming multiple chemically strengthened Li-containing glass samples; and
  - performing acts b) and c) to non-destructively measure the center tension of the multiple glass sample and adjusting the forming of the glass samples so that the center tension falls within a center tension specification.
7. The method according to claim 6, wherein the power-law stress profile is substantially parabolic.
8. A method of measuring a center tension in a chemically strengthened glass sample having a body, a surface and a stress profile that includes a spike region adjacent the sample surface and a deep region that extends from a bottom of the spike region into the glass body, the method comprising:
  - a) measuring a mode spectrum of the glass sample;
  - b) using the mode spectrum, estimating a first contribution to the center tension associated with the spike region and estimating a second contribution to the center

tension due to deep region only, including assuming that the deep region has a power-law stress profile; and

- c) determining a total center tension by adding of the first and second contributions to the center tension.

9. The method according to claim 8, wherein the power-law stress profile is substantially parabolic.

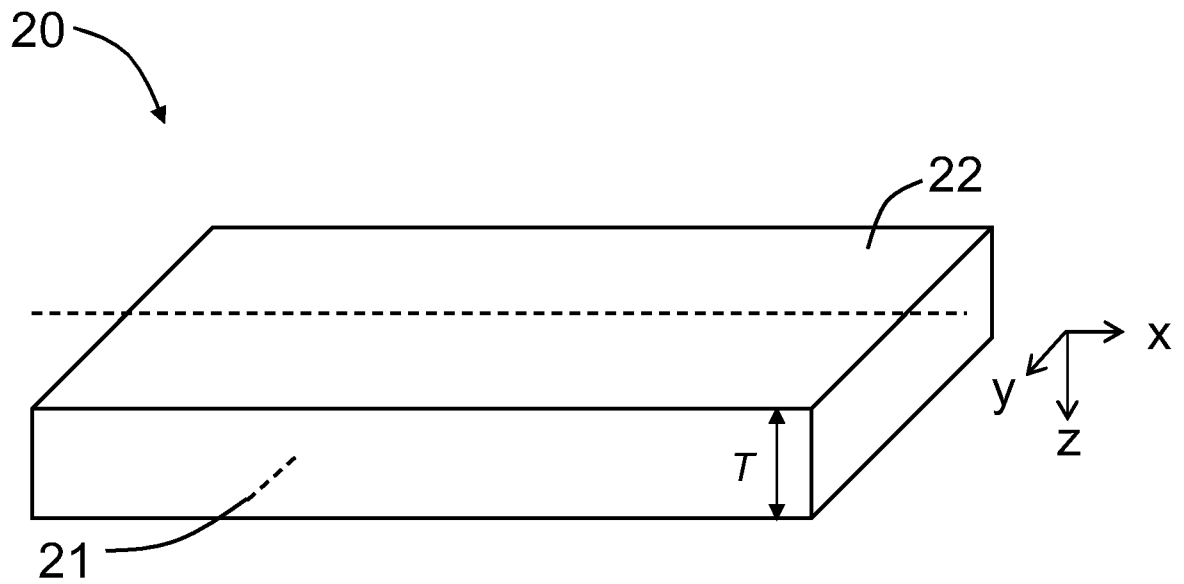
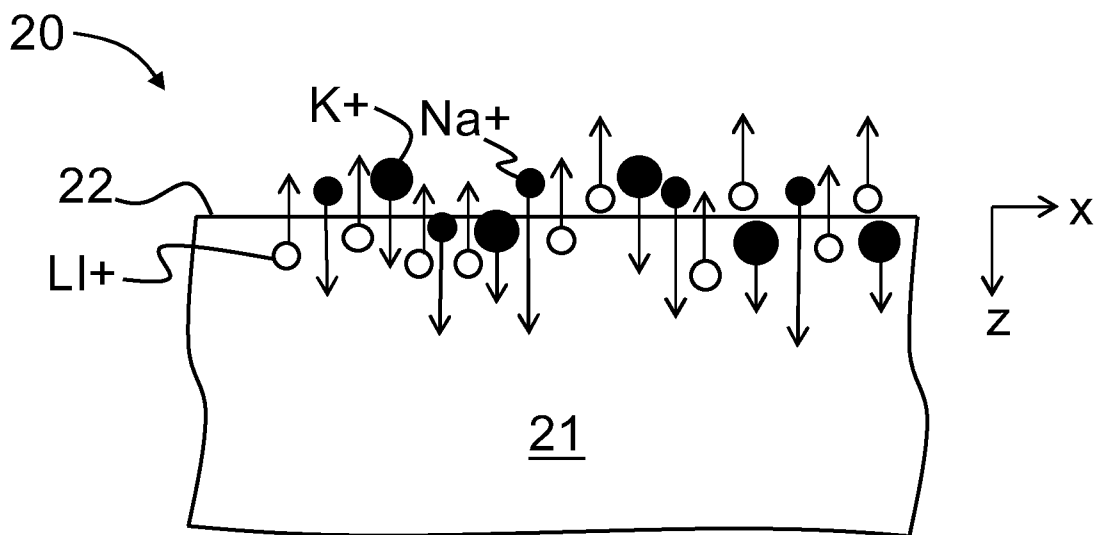
10. The method according to claim 8, wherein stress profile is formed using an ion-exchange of  $\text{Li}^+$  ions in the glass with  $\text{K}^+$  and  $\text{Na}^+$  ions.

11. The method according to claim 8, further comprising performing quality control by comparing the total center tension to a center tension specification

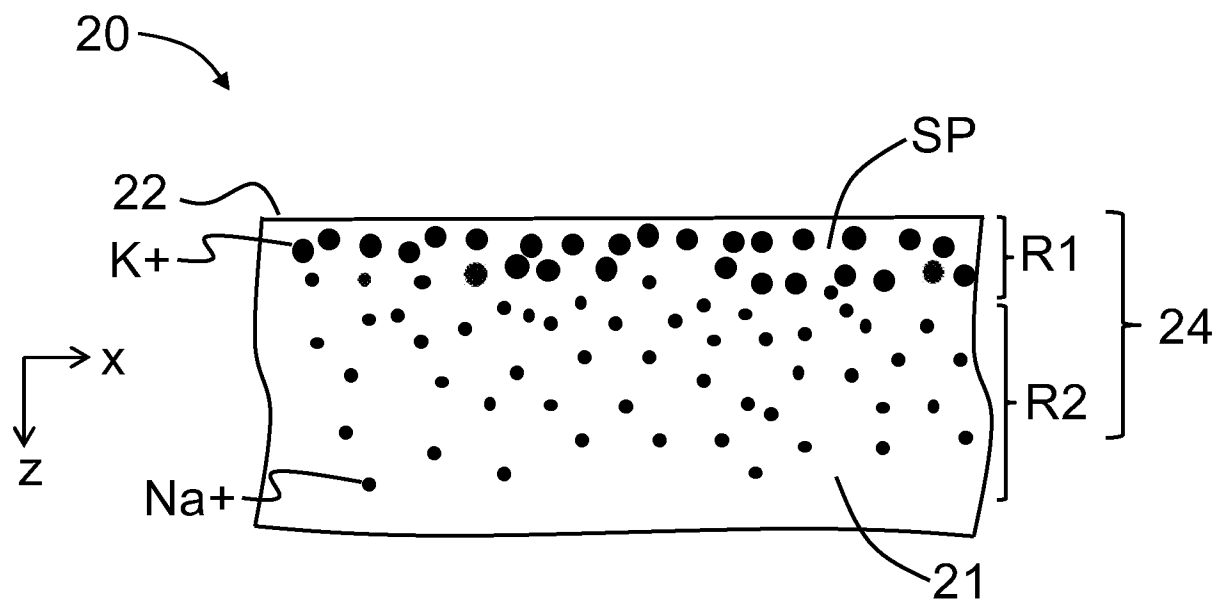
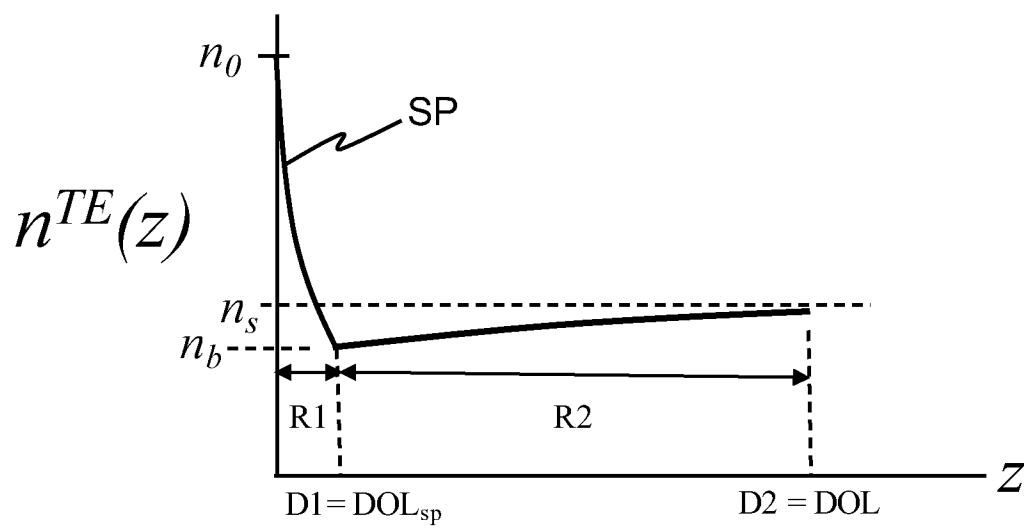
12. The method according to claim 8, wherein measuring the mode spectrum includes capturing the mode spectrum on a photodetector using a prism-coupling system.

13. The method according to claim 8, further including measuring at least one additional stress-related characteristic of the glass sample.

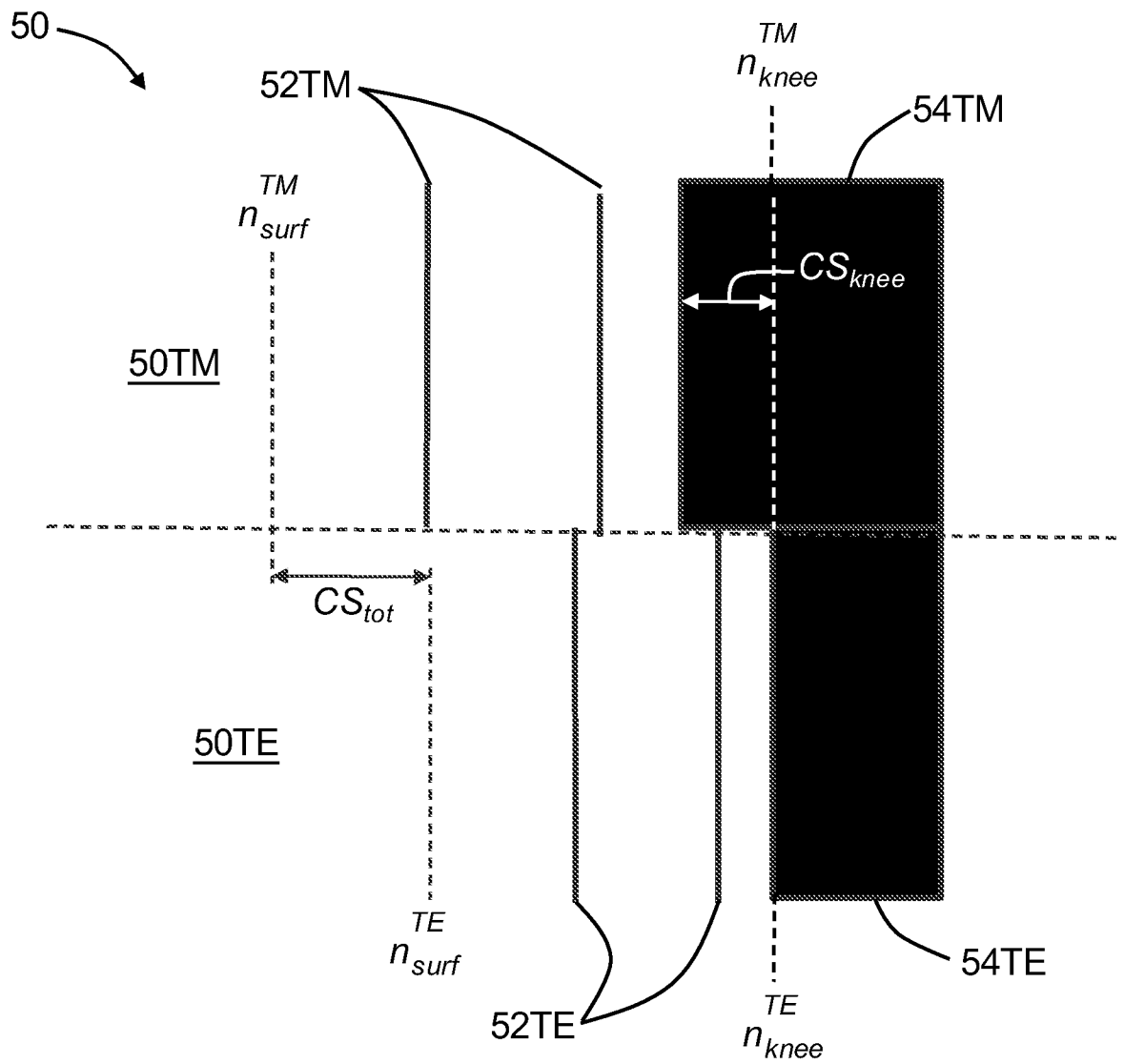
1/7

**FIG. 1A****FIG. 1B**

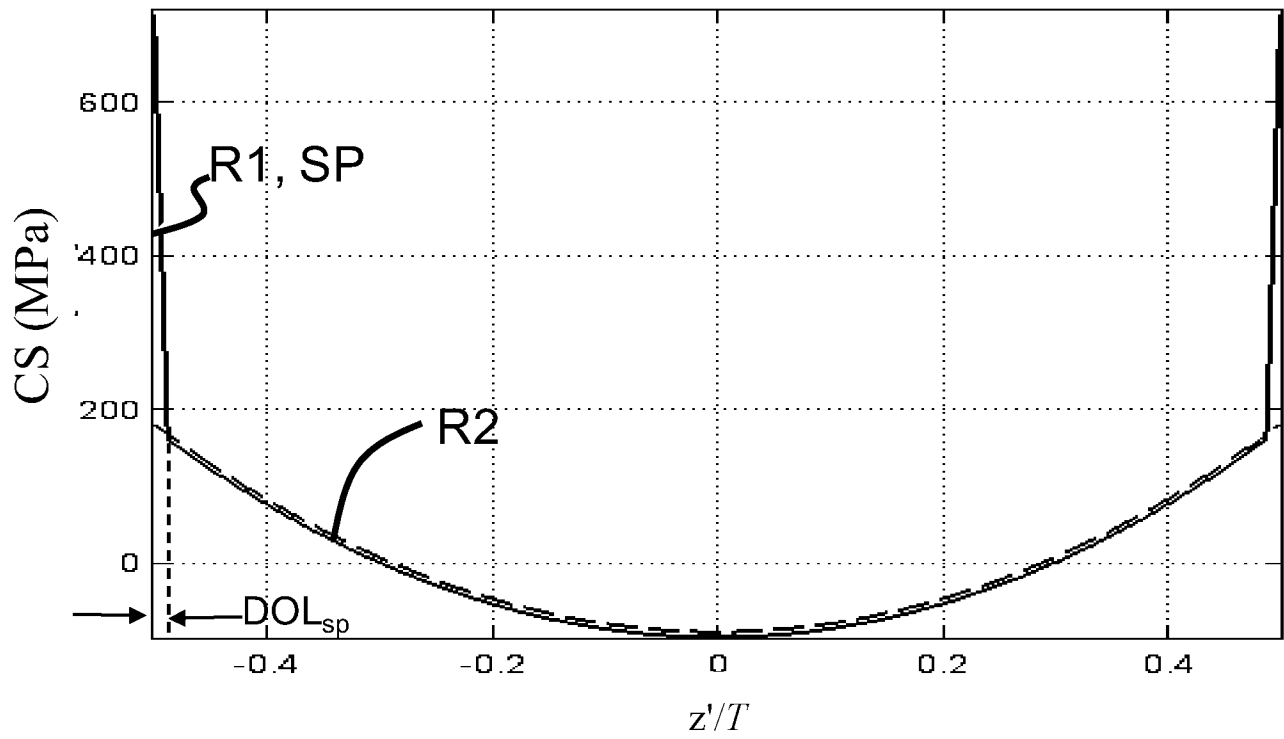
2/7

**FIG. 1C****FIG. 2**

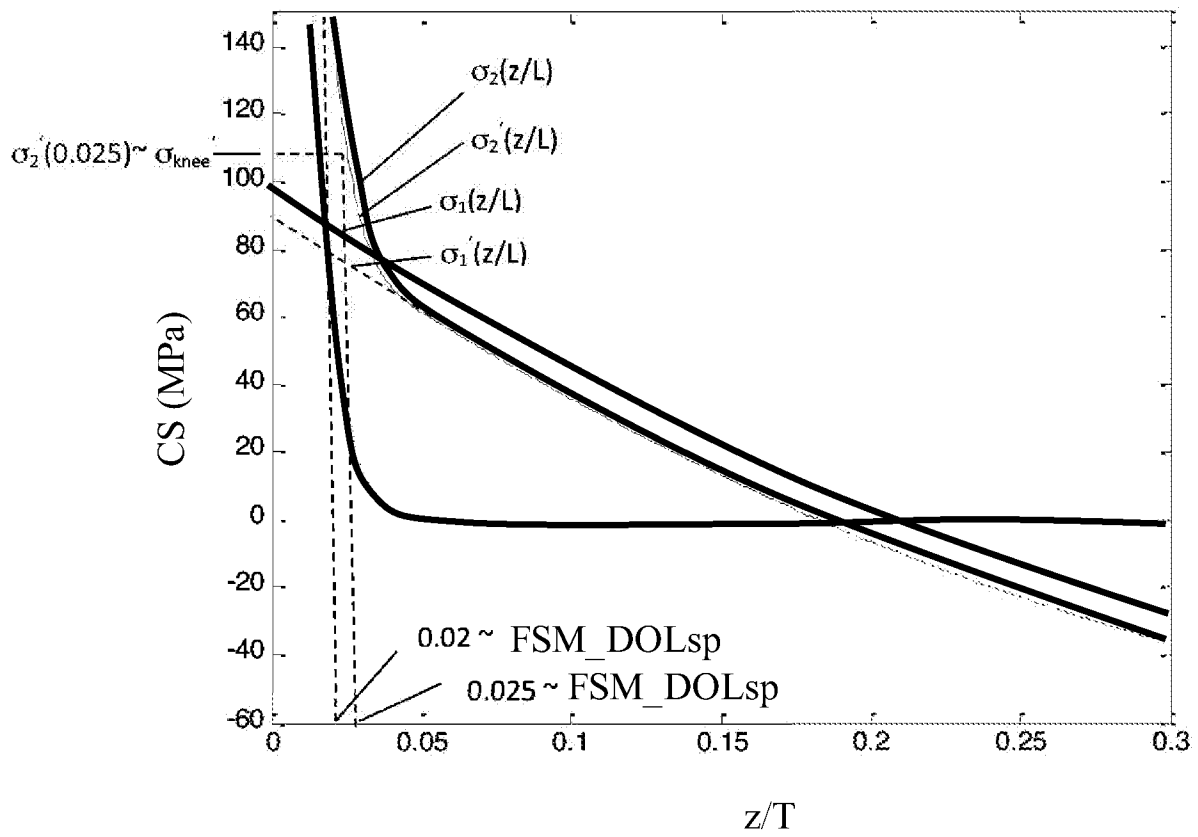
3/7

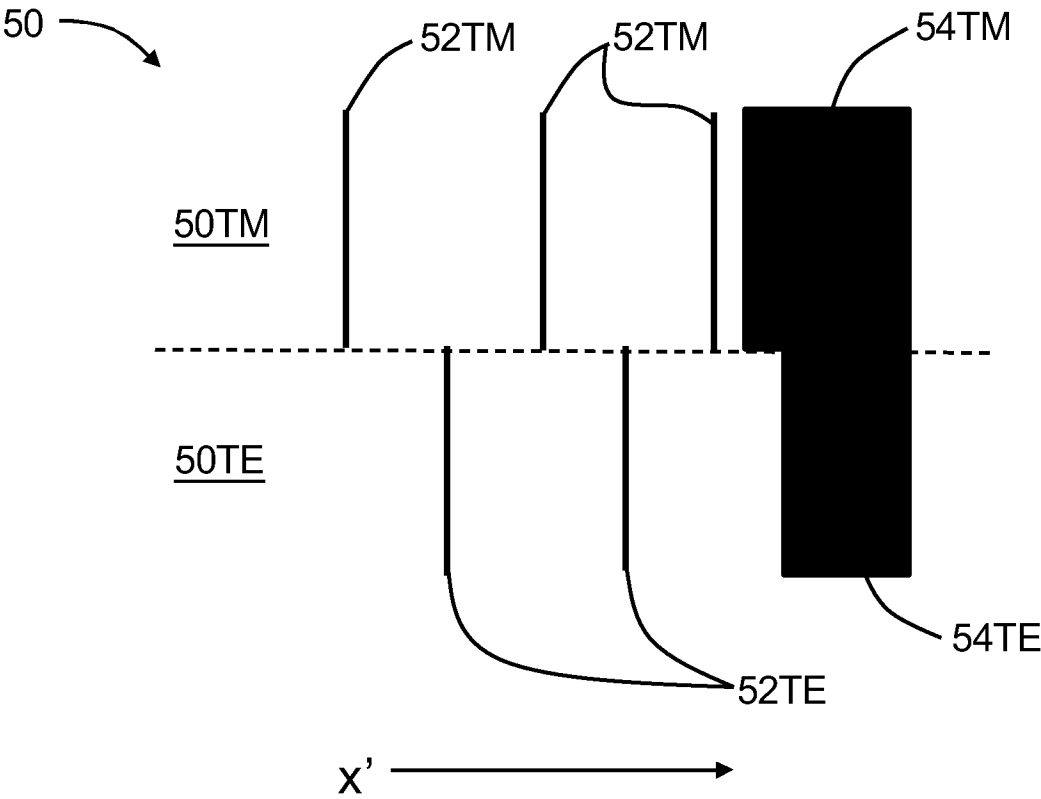
**FIG. 3**

4/7

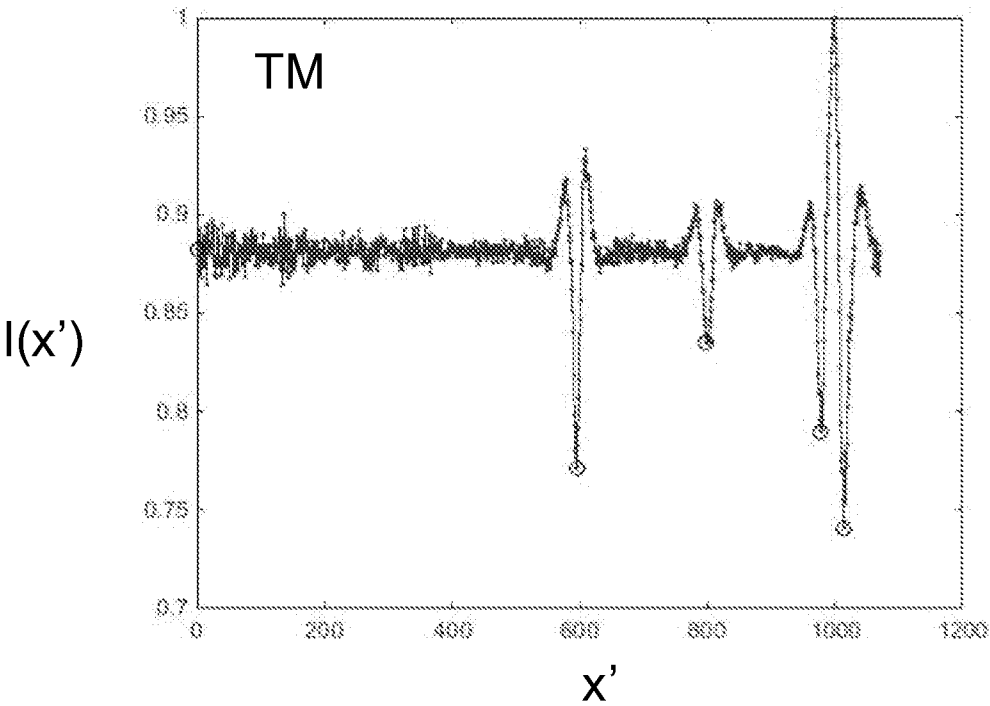
**FIG. 4**

5/7

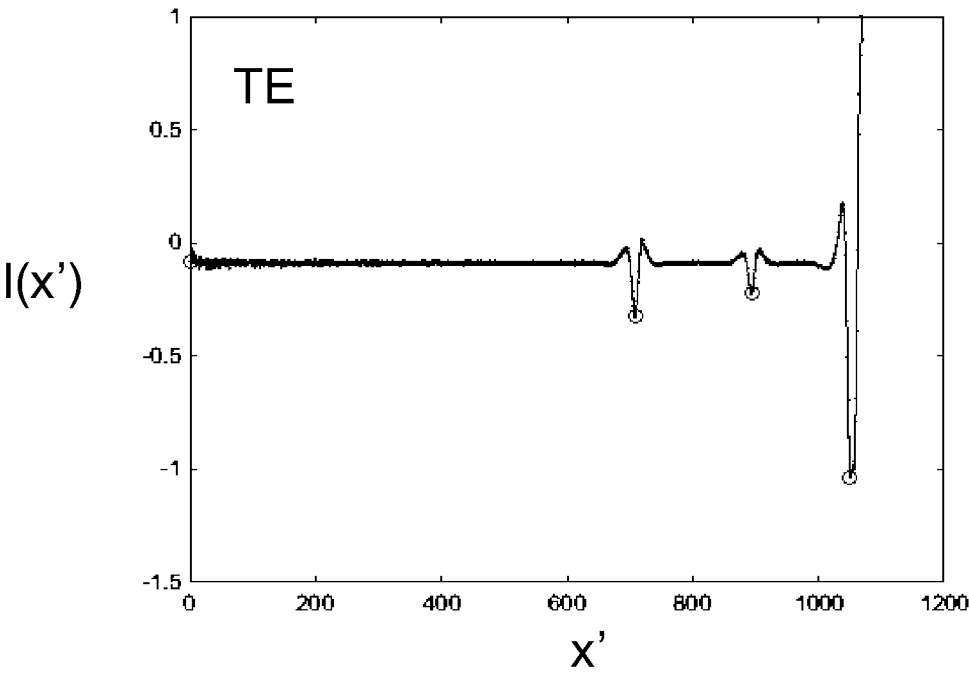
**FIG. 5**



**FIG. 6**



**FIG. 7A**



**FIG. 7B**

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/035449

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. G01N21/958  
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G01N C03C G01L G01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                      | Relevant to claim No. |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | US 2014/368808 A1 (ROUSSEV ROSTISLAV VATCHEV [US] ET AL)<br>18 December 2014 (2014-12-18)<br>cited in the application<br>abstract; figures 1A, 1B, 4A, 4B<br>paragraph [0002] - paragraph [0009]<br>paragraph [0033] - paragraph [0039]<br>paragraph [0060] - paragraph [0063]<br>----- | 1-13                  |
| A         | US 2015/066393 A1 (LIU ANPING [US] ET AL)<br>5 March 2015 (2015-03-05)<br>cited in the application<br>abstract; figure 3B<br>paragraph [0034] - paragraph [0043]<br>-----                                                                                                               | 1-13                  |
| A         | WO 2015/077179 A1 (CORNING INC [US])<br>28 May 2015 (2015-05-28)<br>abstract; figures 1,5<br>-----<br>-/-                                                                                                                                                                               | 1-13                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

19 July 2016

Date of mailing of the international search report

09/09/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040,  
 Fax: (+31-70) 340-3016

Authorized officer

Vorropoulos, G

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/035449

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                 | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | US 2013/224492 A1 (BOOKBINDER DANA CRAIG<br>[US] ET AL) 29 August 2013 (2013-08-29)<br>abstract; figure 3<br>----- | 1-13                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/035449

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| US 2014368808 A1                          | 18-12-2014          | US 2014368808 A1           | 18-12-2014          |
|                                           |                     | US 2015308908 A1           | 29-10-2015          |
| -----                                     |                     |                            |                     |
| US 2015066393 A1                          | 05-03-2015          | CN 105705936 A             | 22-06-2016          |
|                                           |                     | EP 3039408 A1              | 06-07-2016          |
|                                           |                     | KR 20160048926 A           | 04-05-2016          |
|                                           |                     | TW 201514457 A             | 16-04-2015          |
|                                           |                     | US 2015066393 A1           | 05-03-2015          |
|                                           |                     | WO 2015031567 A1           | 05-03-2015          |
| -----                                     |                     |                            |                     |
| WO 2015077179 A1                          | 28-05-2015          | TW 201520178 A             | 01-06-2015          |
|                                           |                     | US 2015147574 A1           | 28-05-2015          |
|                                           |                     | WO 2015077179 A1           | 28-05-2015          |
| -----                                     |                     |                            |                     |
| US 2013224492 A1                          | 29-08-2013          | CN 104870393 A             | 26-08-2015          |
|                                           |                     | EP 2819966 A2              | 07-01-2015          |
|                                           |                     | JP 2015511573 A            | 20-04-2015          |
|                                           |                     | KR 20140131558 A           | 13-11-2014          |
|                                           |                     | TW 201341324 A             | 16-10-2013          |
|                                           |                     | US 2013224492 A1           | 29-08-2013          |
|                                           |                     | US 2016023944 A1           | 28-01-2016          |
|                                           |                     | WO 2013130653 A2           | 06-09-2013          |
| -----                                     |                     |                            |                     |