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(71) Applicant 000232243

Nippon Electric Glass Co., Ltd.

2-7-1, Seiran, Otsu-shi, Shiga-ken

(72) Inventor

Shinkichi MIWA

Nippon Electric Glass Co., Ltd.

2-7-1, Seiran, Otsu-shi, Shiga-ken

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(54) [Title of the Invention] Glass and Glass Substrate for Displays

(57) [Abstract]

[Problem] To provide a glass that satisfies the characteristics required of a display substrate, does not contain arsenic oxide, and is able to reduce bubbles in the glass.

[Solution] Provided is a glass substantially free of arsenic oxide and alkali metal oxides, containing 0.005 to 0.4 mass% SnO₂ and 8 to 13.5 mass% alkaline earth metal oxides (MgO, CaO, SrO, BaO), satisfying the equation $Y_s \leq 0.13X-1$, where the molar content of SnO₂ is Y_s and the molar content of alkaline earth metal oxide is X, and having the following composition: 50 to 70 mass% SiO₂, 10 to 19 mass% Al₂O₃, 5 to 15 mass% B₂O₃, 0 to 3 mass% MgO, 0 to 12 mass% CaO, 0 to 6 mass% SrO, 0 to 5 mass% BaO, 0 to 2 mass% ZnO, 0 to 1 mass% ZrO₂, 0 to 5 mass% TiO₂, 0 to 5 mass% P₂O₅, and 0 to 5 mass% Sb₂O₃.

[Claims]

[Claim 1] A glass substantially free of arsenic oxide and alkali metal oxides, containing 0.005 to 0.4 mass% SnO_2 and 8 to 13.5 mass% alkaline earth metal oxide (MgO , CaO , SrO , BaO), satisfying the equation $Y_s \leq 0.13X-1$, where the molar content of SnO_2 is Y_s and the molar content of alkaline earth metal oxide is X , and having the following composition (mass%):
 50 to 70% SiO_2 ,
 10 to 19% Al_2O_3 ,
 5 to 15% B_2O_3 ,
 0 to 3% MgO ,
 0 to 12% CaO ,
 0 to 6% SrO ,
 0 to 5% BaO ,
 0 to 2% ZnO ,
 0 to 1% ZrO_2 ,
 0 to 5% TiO_2 ,
 0 to 5% P_2O_5 , and
 0 to 5% Sb_2O_3 .

[Claim 2] The glass according to claim 1, wherein the glass contains 0.01 to 0.5 mass% ZrO_2 and satisfies the equation $Y_z \leq 0.13X-1$, where the molar content of ZrO_2 is Y_z and the molar content of alkaline earth metal oxides is X .

[Claim 3] A glass substrate for flat displays, comprising the glass according to claim 1 or 2.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Applicability] The present invention relates to a glass and a glass substrate for displays using this glass, the glass substrate being suitable for use as a flat display substrate for liquid crystal displays and EL displays, etc., and as a glass substrate material for image sensors such as charge-coupled devices (CCDs) and equivalent-pixel contact image sensor (CISs), hard disks, filters, and solar cells.

[0002]

[Prior Art] Glass substrates are widely used as flat display substrates for liquid crystal displays, EL displays, and other devices.

[0003] Electronic devices such as thin-film transistor active matrix liquid crystal displays (TFT-LCDs) are thin and consume little power, and are used in a wide range of applications, including car navigation systems, digital camera viewfinders, and, more recently, computer monitors and televisions.

[0004] Glass substrates used in TFT-LCDs are coated with transparent conductive films, insulating films, semiconductor films, metal films, etc., and various circuits and patterns are formed by photolithography and etching (photoetching) processes. In these film formation and photoetching processes, different

heat treatments and chemical treatments are applied to the glass substrate.

[0005] In general, the TFT array process consists of a series of steps, namely, film formation to resist pattern formation to etching to resist stripping, that are repeated. Etching solutions are selected based on the type of film being processed, and a wide variety of chemical solutions are employed depending on the specific application, such as phosphoric acid solutions for etching Al and Mo-based films, aqua regia ($\text{HCl} + \text{HNO}_3$) solutions for etching ITO-based films, and buffered hydrofluoric acid (BHF) solutions for etching SiN_x and SiO_2 films. In order to reduce costs, these etching solutions are managed using a circulating liquid system rather than being disposable.

[0006] If the chemical resistance of a glass substrate is low, the reaction products produced by the chemical solution and the glass substrate during etching may clog the filters in the circulating liquid system, heterogeneous etching may cause the glass surface to become opaque, and changes in the composition of the chemical solution may cause instability of the etching rate, among other problems. Hydrofluoric acid-based solutions such as BHF strongly corrode glass substrates, making them especially prone to these problems. Therefore, glass substrates of this type must be highly resistant to BHF.

[0007] In addition, it is important that the glass substrate not only have low chemical erosion, but also not undergo any changes in appearance. In other words, it is essential that the glass not undergo any changes such as opacity or roughening due to chemical treatment, as this is a necessary characteristic for display substrates in which transmissivity is important.

[0008] The results of evaluating erosion and appearance changes are not always consistent, especially with regard to BHF resistance. For example, glass with the same erosion rate may or may not undergo changes in appearance after chemical treatment, depending on the composition of the glass.

[0009] Because glass substrates used in TFT-LCDs undergo heat treatment and chemical treatment, they must have the following characteristics.

(1) Because alkali ions diffuse into the semiconductor material during heat treatment when alkali metal oxides are present in the glass, causing deterioration of film properties, the glass must be alkali-free, that is, it must not contain alkali metal oxides.

(2) The glass must have chemical resistance that does not deteriorate due to the acids,

alkalis, and other chemicals used in the photo etching process.

(3) No thermal shrinkage must occur in the glass during heat treatment such as film formation and annealing. To achieve this, the glass must have a high strain point and excellent heat resistance. For example, in the case of polycrystalline silicon (P-Si) TFT-LCD, the processing temperature is 400 to 600°C, so a glass substrate used in this application must have a strain point of 630°C or higher, preferably 650°C or higher.

[0010] Specifically, the processing temperature for P-Si-TFT-LCD production has recently become lower, but it is still higher than that of a-Si-TFT-LCDs. If the heat resistance of the glass substrate is low, when the glass substrate is exposed to high temperatures of 400 to 600°C during the P-Si TFT-LCD production process, minute dimensional shrinkage known as thermal shrinkage occurs, which may cause a shift in the pixel pitch of the TFT, resulting in display defects. If the heat resistance of the glass substrate is too low, deformation or deflection of the glass substrate may occur.

[0011] In addition, for meltability and moldability, the following properties are also required of this type of glass substrate.

(4) Excellent melting properties are required so that melting defects, which are undesirable in a substrate, do not occur in the glass. Specifically, the temperature corresponding to a viscosity of $10^{2.5}$ dPa·s must be below 1650°C, and preferably below 1630°C.

(5) Excellent opacity resistance is required to prevent the appearance of foreign matter during melting and molding in the glass.

[0012] Glass substrates for TFT-LCD are primarily molded using downdraw or float methods. Examples of downdraw methods include the slot downdraw method and the overflow downdraw method. Glass substrates formed using a downdraw method do not require polishing, which has the advantage of making it easier to reduce costs. However, when glass substrates are formed using a downdraw method, glass with excellent opacity resistance is required because glass tends to lose transparency. Specifically, in consideration of the temperature at which glass is formed using the downdraw method, the liquid phase temperature of the glass is preferably less than 1200°C, and more preferably less than 1150°C, and the liquid phase viscosity is preferably less than 10^5 dPa·s, and more preferably $10^{5.5}$ dPa·s.

[0013] In recent years, TFT-LCD panel manufacturers have been working to improve productivity and reduce costs by fabricating multiple devices on glass substrates (base

plates) formed by glass manufacturers, and then cutting each device into a separate unit to obtain products. Moreover, for applications such as TVs and PC monitors, the devices themselves have to be large, and large-area glass substrates of 1000 x 1200 mm are required for multi-sided mounting of these devices.

[0014] Mobile devices such as cell phones and notebook PCs require lightweight devices to make them easier to carry around, and the glass substrate also has to be lightweight. To reduce the weight of glass substrates, making the substrates thinner is effective. Currently, the standard thickness of glass substrates for TFT-LCDs is about 0.7 mm, which is very thin.

[0015] However, large, thin-walled glass substrates such as those mentioned above are subject to significant deflection due to their own weight, which poses a major problem in the manufacturing process.

[0016] After being formed by a glass manufacturer, this type of glass substrate goes through processes such as cutting, slow cooling, inspection, and cleaning. During these processes, glass substrates are loaded and unloaded into cassettes with multiple shelves. These cassettes can hold glass plates horizontally, and two or three sides of a glass substrate can be placed on shelves formed on the two left and right sides, or on the three left, right, and back sides. However, because large, thin glass substrates have a large amount of deflection, some of the glass substrates can easily be damaged by contact with the cassette or other glass substrates when glass substrates are placed in the cassette shelves, or become unstable due to large rocking motions when the glass substrates are removed from the cassette shelves. The same type of cassettes are also used by display manufacturers, resulting in similar problems.

[0017] The amount of deflection due to the weight of the glass substrate itself varies in proportion to the density of the glass and inverse proportion to its Young's modulus. Therefore, to keep the deflection of the glass substrate small, the specific Young's modulus, expressed as the ratio of Young's modulus/density, must be high. To increase the specific Young's modulus, a glass material with a higher Young's modulus and lower density is required. However, for the same specific Young's modulus, glass with a lower density allows for a thicker plate of glass of the same weight. Because the amount of deflection in glass is inversely proportional to the square of the plate thickness, the effect that increasing the plate thickness has on reducing deflection is very significant. Because reducing the density of

glass has a significant effect on reducing the weight of glass, the density of glass should be as low as possible. Specifically, a density of 2.50 g/cm^3 or less, preferably 2.45 g/cm^3 or less, is required.

[0018] This type of alkali-free glass generally contains relatively large amounts of alkaline earth metal oxides. To reduce the density of glass, it is effective to reduce the amount of alkaline earth metal oxides. However, because alkaline earth metal oxides are components that promote the melting properties of glass, reducing the amount reduces the melting properties. When the melting properties of glass are reduced, internal defects such as bubbles and foreign matter are more likely to occur in the glass. Bubbles and foreign particles in glass are fatal defects for display glass substrates because they prevent the transmittance of light. To suppress such internal defects, glass must be melted at high temperatures over a long time.

[0019] However, melting at high temperatures increases the burden on glass melting kilns. For example, refractory materials used in kilns, such as alumina and zirconia, are severely eroded at higher temperatures, shortening the service life of the kiln. Also, since only a limited number of materials can be used at high temperatures, all materials used are more expensive. In addition, the running costs for keeping the interior of a kiln at a constant high temperature are higher than those for glass melted at a low temperature, and melting at a high temperature is very disadvantageous for glass production. For these reasons, there is demand for an alkali-free glass that is able to melt at low temperatures.

[0020] Thermal shock resistance is also an important required property for this type of glass substrate. Even when chamfered, minute scratches and cracks are present on the end faces of the glass substrate, and when tensile stresses caused by heat are concentrated on the scratches and cracks, the glass substrate can sometimes crack. Glass breakage not only reduces the line utilization rate, but there is also a significant risk that the fine glass powder generated during breakage will adhere to glass substrates, causing linear breakage, patterning defects, and other problems.

[0021] Increasing the production speed of TFT-LCDs has become more important recently. This has led to a shortening of the glass substrate heat treatment process, and glass substrates are subjected to more rapid heating and cooling, which tends to further increase the thermal shock to which glass substrates are subjected. Also, as mentioned above, glass substrates are becoming larger, not only making them more

susceptible to temperature differences, but also increasing the probability of micro scratches and cracks on the end surfaces, which increases the probability of substrate destruction during heat processing. The most basic and effective way of solving these problems is to reduce thermal stresses resulting from temperature differences in glass substrates, which demands glass with a low coefficient of thermal expansion. A large difference in thermal expansion between a glass substrate and the TFT materials causes the glass substrate to warp, so the glass substrate must have a coefficient of thermal expansion that approximates the coefficient of thermal expansion of TFT materials such as P-Si (approximately 30 to $33 \times 10^{-7}/^\circ\text{C}$), specifically a coefficient of thermal expansion of 25 to $40 \times 10^{-7}/^\circ\text{C}$, preferably 28 to $35 \times 10^{-7}/^\circ\text{C}$.

[0022]

[Problem to Be Solved by the Invention] Alkali-free glass is generally difficult to melt, and to supply large quantities of high-quality glass substrates at low cost, it is extremely important to improve melting properties of this glass and reduce the defect rate caused by gas bubbles, foreign matter, etc.

[0023] Melting defects in glass, especially gas bubbles in glass, have the greatest impact on yield when producing glass substrates for flat displays. A glass substrate for flat displays is defective if there is even a single gas bubble of 0.1 mm or longer per 1 m^2 of glass substrate. Since gas bubbles in this type of glass substrate extend in the direction that the sheet glass is drawn out during glass molding, even gas bubbles that are very small at the time of melting can easily become 0.1 mm or longer in the glass substrate, making reduction of gas bubbles in molten glass as much as possible the most important challenge.

[0024] Usually, a small amount of a component called a clarifying agent is added to reduce gas bubbles in glass. Typical clarifying agents include sulfates such as sodium sulfate, chlorides such as table salt, arsenite, antimony oxide, and cerium oxide, but because of its extremely high melting temperature, alkali-free glass commonly uses arsenic oxide (As_2O_3 or As_2O_5), which has a significant clarifying effect especially when melted at high temperatures.

[0025] However, arsenic oxide has been designated as a toxic environmental pollutant, and its use and inclusion in glass have become difficult in recent years due to growing environmental concerns.

[0026] In addition to arsenic oxide, stannic dioxide (SnO_2) is another clarifying agent that exhibits clarifying properties at high temperatures. However, SnO_2 has the problem

of crystallizing and causing a loss of transparency during glass molding when present in large quantities in alkali-free glass.

[0027] It is an object of the present invention to provide an alkali-free glass that satisfies the required characteristics for a display substrate and reduces gas bubbles in the glass without containing arsenic oxide.

[0028]

[Means for Solving the Problem] As a result of repeated experiments, the present inventor discovered that in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-RO}$ alkali-free glass, the presence of SnO_2 is essential to sufficiently reduce gas bubbles in the glass without the inclusion of arsenic oxide, and discovered that the amount of SnO_2 that can be incorporated into glass without crystallizing occurring is limited by the amount of alkaline earth metal oxides (MgO , CaO , SrO , BaO) in the glass. The present invention has been proposed on the basis of these discoveries.

[0029] The present invention is a glass substantially free of arsenic oxide and alkali metal oxides, containing 0.005 to 0.4 mass% SnO_2 and 8 to 13.5 mass% alkaline earth metal oxide (MgO , CaO , SrO , BaO), satisfying the equation $Y_s \leq 0.13X-1$, where the molar content of SnO_2 is Y_s and the molar content of alkaline earth metal oxide is X , and having the following composition (mass%):

50 to 70% SiO_2 ,
10 to 19% Al_2O_3 ,
5 to 15% B_2O_3 ,
0 to 3% MgO ,
0 to 12% CaO ,
0 to 6% SrO ,
0 to 5% BaO ,
0 to 2% ZnO ,
0 to 1% ZrO_2 ,
0 to 5% TiO_2 ,
0 to 5% P_2O_5 , and
0 to 5% Sb_2O_3 .

[0030] In the present invention, the glass preferably contains 0.01 to 0.5 mass% ZrO_2 and satisfies the equation $Y_z \leq 0.13X-1$, where the molar content of ZrO_2 is Y_z and the molar content of alkaline earth metal oxides is X .

[0031] The present invention is also a glass substrate for flat displays, comprising the glass described above.

[0032]

[Operation] Alkali earth metal oxides improve the meltability and moldability of glass, but as the amount decreases, the amount of SnO_2 that can be included in the glass also decreases. In other words, the allowable amount of SnO_2 that prevents crystallization of SnO_2 crystals in glass increases as the amount of alkaline earth metal oxides increases. However, if the amount of

alkaline earth metal oxides becomes excessive, the density and thermal expansion coefficient of the glass increase, which is undesirable.

[0033] The present inventor investigated the critical value for the amount of alkaline earth metal oxides that can improve the meltability and moldability of glass, and the critical value for the amount of SnO_2 that can prevent the crystallization of SnO_2 crystals. As a result, he has demonstrated that by including 0.005 to 0.4 mass% of SnO_2 and 8 to 13.5 mass% of alkaline earth metal oxides, and satisfying the equation $Y_s \leq 0.13X-1$, the density and expansion of glass can be reduced while maintaining excellent meltability and moldability, sufficiently reducing the number of gas bubbles in the glass, and suppressing the crystallization of SnO_2 crystals.

[0034] The reasons for limiting the amounts of each component constituting the glass of the present invention will now be explained.

[0035] In the present invention, SnO_2 is a component used as a clarifying agent in place of arsenic oxide, and the amount included is 0.005 to 0.4 mass%. An amount less than 0.005 mass% results in insufficient clarification, and an amount more than 0.4 mass% increases the tendency for SnO_2 crystals to form in the glass. The preferred amount of SnO_2 is from 0.01 to 0.4 mass%.

[0036] The amount of SiO_2 is 50 to 70 mass%. If the amount is less than 50 mass%, chemical resistance, especially acid resistance, deteriorates. In addition, when the amount exceeds 70 mass%, the high-temperature viscosity increases, the meltability deteriorates, and defects such as opaque impurities (cristobalite) are more likely to be present in the glass. The amount of SiO_2 is preferably 55 mass% or more (more preferably 60 mass% or more) and 68 mass% or less (more preferably 66 mass% or less).

[0037] The amount of Al_2O_3 is from 10 to 19 mass%. When the amount is less than 10 mass%, the liquid phase temperature rises, making it easier for cristobalite impurities to form in the glass and causing the strain point to decrease. When the amount exceeds 19 mass%, the buffered hydrofluoric acid resistance of the glass decreases, making the glass surface more susceptible to cloudiness, and the transmissivity of the glass decreases, making the glass more susceptible to mullite and feldspar-type opacity. The amount of Al_2O_3 is preferably 11 mass% or more (more preferably 14 mass% or more) and 18.0 mass% or less.

[0038] B_2O_3 is a component that acts as a melting agent, reducing viscosity and improving meltability. When the amount of B_2O_3 is less

than 5 mass%, its melting action becomes insufficient, and resistance to buffered hydrofluoric acid deteriorates. When the amount exceeds 15 mass%, the strain point of the glass decreases, resulting in reduced heat resistance and a deterioration in acid resistance. The amount of B_2O_3 is preferably 7 mass% or more (more preferably 8.6 mass% or more) and 14 mass% or less (more preferably 12 mass% or less).

[0039] MgO reduces the high-temperature viscosity and improves glass meltability without lowering the strain point. Among alkaline earth metal oxides, it has the least effect on increasing density. However, when present in large amounts, the liquid phase temperature rises and opacity resistance decreases. In addition, MgO reacts with buffered hydrofluoric acid to form products that may adhere to elements on the glass substrate surface or adhere to the glass substrate itself and cause it to become cloudy. For these reasons, the amount included is restricted. The amount of MgO is 0 to 3 mass%, preferably 0 to 1 mass%, more preferably 0 to 0.5 mass%, and ideally substantially absent.

[0040] CaO , like MgO , is a component that lowers high-temperature viscosity and significantly improves glass meltability without reducing the strain point, and the amount included is 0 to 12 mass%. When the amount of CaO exceeds 12 mass%, the buffered hydrofluoric acid resistance of the glass deteriorates, making the glass substrate surface susceptible to erosion. Additionally, reaction products adhere to the glass substrate surface, causing the glass to become cloudy. Furthermore, the density and thermal expansion coefficient of the glass increase too much, which is undesirable. The amount of CaO is preferably 4 mass% or more (more preferably 5 mass% or more) and 10 mass% or less (more preferably 9 mass% or less).

[0041] SrO is a component that improves the chemical resistance of glass and improves its opacity, but when included in large amounts, reduces meltability and increases the density and thermal expansion coefficient of glass, which is undesirable. The amount of SrO is 0 to 6 mass%.

[0042] BaO is also a component that improves the chemical resistance and light transmission of glass, but when included in large amounts, reduces meltability and increases the density and thermal expansion coefficient of glass, which is undesirable. The amount of BaO is 0 to 5 mass%.

[0043] Alkali earth metal oxides such as MgO , CaO , BaO , and SrO lower the liquid phase

temperature of glass and make it difficult for crystalline impurities to form in the glass, thereby improving the meltability and moldability of glass. To prevent SnO_2 opacity, the inclusion of alkaline earth metal oxides is essential. However, excessive amounts can increase the glass density to over 2.50 g/cm^3 and raise the thermal expansion coefficient to over $40 \times 10^{-7}/^\circ\text{C}$. Therefore, the total content must be limited to 8 to 13.5 mass%. A more desirable range is from 8 to 13 mass%.

[0044] ZnO is a component that improves the resistance of glass substrates to buffer hydrofluoric acid and improves meltability, but when present in an amount of 2 mass% or more, the glass becomes prone to opacity. This amount is also undesirable because it reduces distortion. The preferred amount of ZnO is from 0 to 1 mass%.

[0045] ZrO_2 is a component that improves the chemical resistance of glass, particularly acid resistance. However, when the amount exceeds 1 mass%, the liquid phase temperature rises, making zirconium impurities more likely to appear, which is undesirable. The preferred amount ZrO_2 is from 0 to 0.5 mass%.

[0046] Note that ZrO_2 may be present in an amount of 0.01 mass% or more without being added as a raw material, as it may be inadvertently mixed in from refractory materials in the melting furnace. There is a close relationship between the amount of ZrO_2 and SnO_2 opacity. As the ZrO_2 content increases, it becomes more likely to cause significant SnO_2 opacity, so it is desirable to keep the ZrO_2 content as low as possible. To suppress SnO_2 opacity caused by ZrO_2 , the amount of ZrO_2 is preferably kept below 0.5 mass% and the amount of alkaline earth metal oxides is restricted. Specifically, the equation $Yz \leq 0.13X-1$ is preferably satisfied, where Yz is the molar content of ZrO_2 and X is the molar content of alkaline earth metal oxides.

[0047] TiO_2 is a component that improves the chemical resistance of glass, particularly acid resistance, and reduces high-temperature viscosity to enhance meltability. However, when present in high concentrations, it causes discoloration of glass and reduces its transmissivity, making it unsuitable for use as in glass substrate for displays. Therefore, TiO_2 should be limited to 0 to 5 mass%, preferably 0 to 2 mass%.

[0048] P_2O_5 is a component that improves the opacity-resistance of glass when added in small amounts, but when present in large amounts, it causes phase separation and opacity in glass and significantly reduces acid resistance, making it undesirable. Therefore, P_2O_5 should

be limited to 0 to 5 mass%, preferably 0 to 4 mass%.

[0049] In addition to the components mentioned above, the present invention may contain Y_2O_3 , Nb_2O_3 , and La_2O_3 in amounts of up to about 5 mass%. These components have the effect of increasing the strain point and Young's modulus, but excessive amounts increases the density of the glass, which is undesirable.

[0050] Sb_2O_3 , Sb_2O_5 , F, Cl, and SO_3 are all components that promote the clarifying effect when used in combination with SnO_2 . Sb_2O_3 and Sb_2O_5 , in particular, have a significant effect, but excessive amounts increases the density of the glass, which is undesirable. Therefore, Sb_2O_3 and Sb_2O_5 should be limited to 5 mass% or less, preferably 3 mass% or less, in terms of Sb_2O_3 . Cl also has a significant effect on improving and promoting the meltability of glass and can be included up to an amount of 1 mass%. Therefore, in the present invention, when SnO_2 is co-present with Sb_2O_3 or Sb_2O_5 and Cl, glass with excellent bubble qualities is easily obtained. Other clarifying agents and components can be present within ranges that do not adversely affect the properties of the glass.

[0051] Note that CeO_2 also acts as a clarifying agent, but it should be avoided because it reduces the transmissivity of glass. Specifically, the amount should be kept below 0.01 mass%. Colorant components such as Cr, Ni, Co, and Mo should also be avoided as they reduce the transmissivity of glass. Specifically, the amount should be kept below 0.01 mass%.

[0052] In addition, the glass of the present invention is substantially free of arsenic oxide and alkali metal oxides for the reasons described above. Note that "substantially free" in the present invention means that something is present only as an impurity and is not intentionally included in the glass raw material. Specifically, the amounts of arsenic oxide and alkali metal oxides should be kept to 0.05 mass% or less, preferably 0.02 wt% or less, and more preferably 0.01 wt% or less.

[0053]

[Examples] The following is a detailed description of the present invention with reference to the examples.

[0054] Tables 1 to 5 show glass of the present invention (Samples No. 1 to 9) and comparative glass (Samples No. 10 to 14). In the tables, MCSB denotes the total amount of alkaline earth metal oxides, and X denotes the molar content of alkaline earth metal oxides.

[0055]

[Table 1]

Sample Composition	No. 1		No. 2		No. 3	
	mass%	mol%	mass%	mol%	mass%	mol%
SiO ₂	60.5	67.92	60.5	67.91	60.6	68.37
Al ₂ O ₃	15.0	9.92	15.0	9.92	15.0	9.97
B ₂ O ₃	10.0	9.69	10.0	9.69	10.5	10.23
MgO	-	-	-	-	-	-
CaO	5.5	6.62	5.5	6.62	5.5	6.65
SrO	5.1	3.31	5.0	3.25	4.0	2.62
BaO	2.0	0.88	2.0	0.88	2.0	0.88
ZnO	0.5	0.41	0.5	0.41	1.0	0.83
ZrO ₂	0.15	0.08	0.2	0.11	0.3	0.17
TiO ₂	-	-	-	-	-	-
SnO ₂	0.25	0.11	0.3	0.13	0.1	0.04
P ₂ O ₅	-	-	-	-	-	-
Sb ₂ O ₃	0.5	0.12	0.5	0.12	1.0	0.23
Cl	0.5	0.96	0.5	0.96	-	-
MCSB	12.5	10.81	12.5	10.75	11.5	10.15
0.13 x X-1		0.41		0.40		0.32
Density (g/cm ³)	2.45		2.45		2.45	
Thermal Expansion Coefficient (x 10 ⁻¹ /°C)	35		34		35	
Stress Point	661°C		662°C		660°C	
10 ^{2.5} dPa · s	1585°C		1586°C		1587°C	
Liquid Phase Temperature	1070°C		1063°C		1066°C	
SnO ₂ Opacity	No		No		No	
HCl Resistance Amount of Corrosion Appearance	2.8 μm ○		2.7 μm ○		2.8 μm ○	
BHF Resistance Amount of Corrosion Appearance	0.7 μm ○		0.7 μm ○		0.7 μm ○	
Bubble Retention	○		○		○	

[0056]

[Table 2]

Sample Composition	No. 4		No. 5		No. 6	
	mass%	mol%	mass%	mol%	mass%	mol%
SiO ₂	60.5	68.28	64.0	69.84	62.3	68.41
Al ₂ O ₃	15.0	9.98	16.0	10.29	16.0	10.35
B ₂ O ₃	9.6	9.35	10.0	9.42	11.0	10.42
MgO	-	-	-	-	-	-
CaO	6.0	7.26	8.0	9.35	8.1	9.53
SrO	3.0	1.96	1.0	0.63	0.5	0.32
BaO	2.0	0.88	0.5	0.21	0.5	0.22
ZnO	-	-	-	-	-	-
ZrO ₂	0.4	0.22	0.3	0.16	0.2	0.11
TiO ₂	-	-	-	-	-	-
SnO ₂	0.4	0.18	0.2	0.09	0.01	0
P ₂ O ₅	2.0	0.96	-	-	-	-
Sb ₂ O ₃	0.7	0.16	-	-	1.19	0.27
Cl	0.4	0.77	-	-	0.2	0.37
MCSB	11.0	10.10	9.5	10.19	9.1	10.07
0.13 x X-1		0.31		0.33		0.31
Density (g/cm ³)	2.43		2.37		2.38	
Thermal Expansion Coefficient (x 10 ⁻¹ /°C)	35		34		32	
Stress Point	665°C		675°C		670°C	
10 ^{2.5} dPa · s	1595°C		1610°C		1600°C	
Liquid Phase Temperature	1069		1040°C		1090°C	
SnO ₂ Opacity	No		No		No	
HCl Resistance Amount of Corrosion Appearance	2.6 μm ○		2.0 μm ○		2.2 μm ○	
BHF Resistance Amount of Corrosion Appearance	0.7 μm ○		0.7 μm ○		0.6 μm ○	
Bubble Retention	○		○		Δ	

[0057]

[Table 3]

Sample Composition	No. 7		No. 8		No. 9	
	mass%	mol%	mass%	mol%	mass%	mol%
SiO ₂	62.0	68.62	61.2	66.61	60.0	67.72
Al ₂ O ₃	16.0	10.44	17.0	10.90	14.0	9.31
B ₂ O ₃	10.5	10.03	8.0	7.52	11.0	10.72
MgO	-	-	2.0	3.24	-	-
CaO	8.0	9.49	6.0	7.00	6.5	7.86
SrO	0.8	0.51	4.0	2.52	2.3	1.51
BaO	0.5	0.22	0.5	0.21	1.5	0.66
ZnO	-	-	-	-	0.7	0.58
ZrO ₂	0.4	0.22	0.15	0.08	0.45	0.25
TiO ₂	-	-	-	-	0.	0.42
SnO ₂	0.3	0.13	0.15	0.07	0.05	0.02
P ₂ O ₅	-	-	-	-	1.0	0.48
Sb ₂ O ₃	1.5	0.34	-	-	2.0	0.47
Cl	-	-	1.0	1.84	-	-
MCSB	9.3	10.22	12.5	12.97	10.3	10.03
0.13 x X-1		0.33		0.69		0.30
Density (g/cm ³)	2.39		2.44		2.45	
Thermal Expansion Coefficient (x 10 ⁻¹ /°C)	33		35		34	
Stress Point	669°C		693°C		650°C	
10 ^{2.5} dPa · s	1603°C		1619°C		1539°C	
Liquid Phase Temperature	1042°C		1089°C		1065°C	
SnO ₂ Opacity	No		No		No	
HCl Resistance Amount of Corrosion Appearance	1.8 μm ○		0.1 μm ○		0.8 μm ○	
BHF Resistance Amount of Corrosion Appearance	0.7 μm ○		0.6 μm Δ		0.7 μm ○	
Bubble Retention	○		○		○	

[0058]

[Table 4]

Sample Composition	No. 10		No. 11		No. 12	
	mass%	mol%	mass%	mol%	mass%	mol%
SiO ₂	59.0	67.56	58.5	67.15	59.5	67.53
Al ₂ O ₃	15.0	10.12	15.0	10.15	15.0	10.03
B ₂ O ₃	10.0	9.88	10.0	9.91	10.0	9.80
MgO	-	-	-	-	-	-
CaO	5.0	6.14	5.0	6.15	6.0	7.30
SrO	6.0	3.98	6.0	3.99	6.0	3.95
BaO	3.0	1.35	3.0	1.35	2.0	0.89
ZnO	-	-	-	-	-	-
ZrO ₂	0.5	0.28	1.5	0.84	0.5	0.28
TiO ₂	-	-	-	-	-	-
SnO ₂	1.5	0.68	1.0	0.46	-	-
P ₂ O ₅	-	-	-	-	-	-
Sb ₂ O ₃	-	-	-	-	1.0	0.23
Cl	-	-	-	-	-	-
MCSB	14.0	11.47	14.00	11.49	14.00	12.14
0.13 x X-1		0.49		0.49		0.58
Density (g/cm ³)	2.52		2.51		2.52	
Thermal Expansion Coefficient (x 10 ⁻¹ /°C)	38		38		37	
Stress Point	662°C		665°C		659°C	
10 ^{2.5} dPa · s	1579°C		1544°C		1555°C	
Liquid Phase Temperature	1275°C		1252°C		1072°C	
SnO ₂ Opacity	Yes		Yes		No	
HCl Resistance Amount of Corrosion Appearance	2.0 μm ○		1.8 μm ○		2.2 μm ○	
BHF Resistance Amount of Corrosion Appearance	0.7 μm ○		0.7 μm ○		0.7 μm ○	
Bubble Retention	○		○		X	

[0059]

[Table 5]

Sample Composition	No. 13		No. 14	
	mass%	mol%	mass%	mol%
SiO ₂	49.0	58.73	72.0	78.45
Al ₂ O ₃	15.0	10.60	15.0	9.63
B ₂ O ₃	17.0	17.59	4.5	4.23
MgO	0.3	0.54	1.5	2.44
CaO	4.0	5.14	3.0	3.50
SrO	3.0	2.09	-	-
BaO	10.0	4.70	3.0	1.28
ZnO	-	-	-	-
ZrO ₂	0.5	0.29	0.3	0.16
TiO ₂	-	-	-	-
SnO ₂	0.2	0.10	0.7	0.30
P ₂ O ₅	-	-	-	-
Sb ₂ O ₃	1.0	0.25	-	-
Cl	-	-	-	-
MCSB	17.3	12.47	7.5	7.22
0.13 x X-1		0.62		-0.06
Density (g/cm ³)	2.56		2.34	
Thermal Expansion Coefficient (x 10 ⁻¹ /°C)	41		22	
Stress Point	615°C		712°C	
10 ^{2.5} dPa · s	1380°C		1945°C	
Liquid Phase Temperature	1030°C		1420°C	
SnO ₂ Opacity	No		Yes	
HCl Resistance Amount of Corrosion Appearance	2.2 μm X		0.1 μm ○	
BHF Resistance Amount of Corrosion Appearance	0.7 μm ○		0.8 μm X	
Bubble Retention	○		○	

[0060] Each glass sample in the table was prepared as follows.

[0061] First, batches of glass raw materials were mixed to form the compositions in each table, and the mixtures were placed in platinum crucibles, melted at 1600°C for 24 hours, and poured onto carbon plates to form glass plates. The glass samples obtained in this manner were subjected to various tests to determine their density, thermal expansion coefficient, strain point, 10^{2.5} dPa·s temperature, liquid phase temperature, presence or absence of SnO₂ opacity, HCl resistance, and BHF resistance. The results are shown in the tables.

[0062] As can be seen in the tables, the glass in Samples No. 1 to No. 9, which are examples of the present invention, have a density of 2.45 g/cm³ or less and a thermal expansion coefficient of 35 × 10⁻⁷/°C or less, resulting in a weight reduction and excellent thermal impact resistance. In addition, due to a high strain point of 650°C or higher, thermal shrinkage was low, and the temperature at 10^{2.5} dPa·s was 1619°C or lower. The liquid phase temperature was

1090°C or lower, and no SnO₂ opacity was observed at the glass-platinum interface. The samples also had excellent HCl and BHF resistance, and bubble release properties.

[0063] In contrast, Samples No. 10 and 11, which are comparative examples, had a high density and liquid phase temperature, and a large amount of SnO₂ opacity at the glass-platinum interface. Sample No. 12 had high density and poor bubble release properties. Sample No. 13 had high density and thermal expansion coefficient, low strain point, and poor HCl resistance. Sample No. 14 had a high 10^{2.5} dPa·s temperature and liquid phase temperature, and SnO₂ opacity was observed. Its appearance also changed due to the BHF solution.

[0064] The densities in the tables were measured using the well-known Archimedes method. The thermal expansion coefficient was the average thermal expansion coefficient in the temperature range of 30 to 380°C as measured using a dilatometer.

[0065] The strain point was measured based on ASTM C336-71. A higher value indicates glass with higher heat resistance.

[0066] The $10^{2.5}$ dPa·s temperature is the temperature at the high-temperature viscosity of $10^{2.5}$ poises, and was measured using the well-known platinum ball pull-up method. A lower value indicates better meltability.

[0067] The liquid phase temperature was measured by grinding each glass sample, passing it through a standard 30-mesh (500 μ m) sieve, placing the glass powder remaining in the 50-mesh (300 μ m) sieve into a platinum boat, holding it in a temperature gradient furnace for 24 hours, removing the platinum boat, and then observing the glass sample under a microscope to determine the temperature at which opacity (crystalline impurities) occurred in the glass.

[0068] The SnO₂ opacity was evaluated using the following method. SnO₂ opacity tends to precipitate at the interface of glass with a refractory material or at the interface with platinum. The platinum-glass interface of the glass samples whose liquid phase temperature had been measured were observed under a microscope. Those in which SnO₂ crystals were observed at temperatures of 1050°C or higher were assigned "Yes" and those in which no crystals were observed were assigned "No" in the tables.

[0069] BHF resistance and HCl resistance were evaluated using the following method. First, both sides of each glass sample were optically polished, a portion was masked, and the samples were immersed in a solution of a predetermined concentration at a specified temperature for a specified time. After the chemical treatment, the mask was removed and the difference in height between the mask and the etched area was measured using a surface roughness tester. The measured value was recorded as the amount of etching. After optically polishing both sides of each glass sample, the glass samples were immersed in a solution of a predetermined concentration at a specified temperature for a specified time, and then the glass surfaces were visually inspected. Glass surfaces that were cloudy, rough, or cracked were assigned an "X," those with slight cloudiness were assigned an " Δ ," and those with no changes were assigned an "O."

[0070] As for the chemical solution and treatment conditions, the amount of corrosion resistance to BHF was measured using a 130 BHF solution (NH₄HF: 4.6 mass%, NH₄F: 36 mass%) at 20°C for 30 minutes. The evaluation of appearance was conducted using

a 63 BHF solution (HF: 6 mass%, NH₄F: 30 mass%) at 20°C for 30 minutes. The amount of corrosion resistance to HCl was measured using a 10 mass% hydrochloric acid aqueous solution at 80°C for 24 hours. The evaluation of appearance was performed using a 10% hydrochloric acid solution at 80°C for 3 hours.

[0071] The number of bubbles was measured by counting the number of bubbles (0.1 mm or longer) in a glass sample, and assigning "X" to samples with more than 100 bubbles per 100 g of glass, " Δ " to samples with 10 to 100 bubbles, and "O" to samples with fewer than 10 bubbles.

[0072] The glass in Sample No. 1, which is an example of the present invention, was melted in a test melting furnace and molded using the overflow down-draw method to produce a 0.5 mm thick display glass substrate. The substrate met the specifications for bubble quality and did not exhibit any loss of transparency. The warping of the glass substrate was 0.075% or less, the waviness (WCA) was 0.15 μ m or less (cut-off fh: 0.8 mm, fl: 8 mm), and the surface roughness (Ry) was 100 Å or less (cut-off λ c: 9 μ m). The glass substrate exhibited excellent surface precision and was suitable for use as a glass substrate for liquid crystal displays.

[0073]

[Effects of the Invention] As described above, the glass in the present invention has (1) a density of 2.50 g/cm³ or less, (2) a coefficient of thermal expansion of 25 to 40 $\times 10^{-7}/^{\circ}\text{C}$, (3) a strain point of 630°C or more, (4) a temperature of $10^{2.5}$ dPa·s of 1650°C or less, (5) a liquid phase temperature of 1200°C or less, (6) no SnO₂ crystal precipitation, (7) little change in the amount of erosion and appearance due to treatment with a specified BHF solution, and (8) little change in the amount of erosion and appearance due to treatment with a specified HCl solution. Because the glass in the present invention satisfies all of these required characteristics for use as a glass substrates for TFT-LCDs, is substantially free of arsenic oxide and alkali metal oxides, and can be formed using the downdraw method, high-quality glass substrates with low environmental impact and low cost can be obtained that are particularly suitable for use as glass substrates for liquid crystal displays.

[0074] The glass of the present invention is also suitable for use as a glass substrate for flat display panels such as EL displays, image sensors such as CCDs and CISs, hard disks, filters, and solar cells.

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F Terms (Reference) 2H090 HC15 JB02 JC13 JC19 JD09 JD13 JD17 LA04
4G062 AA01 BB01 DA06 DB04 DC03 DC04 DD01 DD02 DD03 DE01 DE02 DE03
DF01 EA01 EB01 EC01 ED01 ED02 EE01 EE02 EE03 EE04 EF01 EF02
EF03 EG01 EG02 EG03 FA01 FB01 FC01 FC02 FD01 FE02 FF01 FG01
FH01 FJ01 FK01 FL01 GA01 GA10 GB01 GC01 GD01 GE01 HH01 HH03
HH05 HH07 HH09 HH11 HH13 HH15 HH17 HH20 JJ01 JJ03 JJ04 JJ05
JJ07 JJ10 KK01 KK03 KK05 KK07 KK10 MM27 NN34