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

(57) [Abstract]

[Objective] To provide an alkali-free glass suitable for use as a glass substrate for P-Si TFT-LCDs, which satisfies the required properties for TFT-LCD glass substrates, is lightweight, exhibits minimal deflection, and has a thermal expansion coefficient of $25\text{--}36 \times 10^{-7}/^{\circ}\text{C}$.

[Composition] The glass has a composition, expressed in mass percentage, comprising: SiO₂: 58–70%, Al₂O₃: 10–19%, B₂O₃: 6.5–15%, MgO: 0–2%, CaO: 3–12%, BaO: 0.1–5%, SrO: 0–4%, BaO+SrO: 0.1–6%, ZnO: 0–5%, MgO+CaO+BaO+SrO+ZnO: 5–15%, ZrO₂: 0–5%, TiO₂: 0–5%, P₂O₅: 0–5%, and is substantially free of alkali metal oxides. The glass has a density of 2.45g/cm³ or less, an average thermal expansion coefficient of $25\text{--}36 \times 10^{-7}/^{\circ}\text{C}$ in the temperature range of 30–380°C, and a strain point of 640°C or higher.

[Scope of Claims]

[Claim 1] An alkali-free glass having a composition, expressed in mass percentage, comprising SiO₂: 58–70%, Al₂O₃: 10–19%, B₂O₃: 6.5–15%, MgO: 0–2%, CaO: 3–12%, BaO: 0.1–5%, SrO: 0–4%, BaO+SrO: 0.1–6%, ZnO: 0–5%, MgO+CaO+BaO+SrO+ZnO: 5–15%, ZrO₂: 0–5%, TiO₂: 0–5%, P₂O₅: 0–5%, and being substantially free of alkali metal oxides, characterized in that the glass has a density of 2.45g/cm³ or less, an average thermal expansion coefficient of 25–36×10⁻⁷/°C in the temperature range of 30–380°C, and a strain point of 640°C or higher.

[Claim 2] The alkali-free glass according to Claim 1, characterized in that the mass ratio (BaO+SrO)/BaO is 1.1–10.

[Claim 3] The alkali-free glass according to Claim 1, characterized in that the liquidus temperature is 1,150°C or lower, and the viscosity at the liquidus temperature is 10^{5.4} dPa·s or higher.

[Claim 4] The alkali-free glass according to Claim 1, characterized in that, when treated with a 10% HCl aqueous solution at 80°C for 24 hours, the erosion is 10 μm or less, and when treated with a 10% HCl aqueous solution at 80°C for 3 hours, no cloudiness or surface roughness is observed by visual surface inspection.

[Claim 5] The alkali-free glass according to Claim 1, characterized in that, when treated with a 130BHF solution at 20°C for 30 minutes, the erosion is 0.8 μm or less, and when treated with a 63BHF solution at 20°C for 30 minutes, no cloudiness or surface roughness is observed by visual surface inspection.

[Claim 6] The alkali-free glass according to Claim 1, characterized in that the specific Young's modulus is 27.5 GPa/g·cm⁻³ or higher.

[Claim 7] The alkali-free glass according to Claim 1, characterized in that it is free of As₂O₃ and contains Sb₂O₃+Sb₂O₅+SnO₂+Cl in an amount of 0.5–3.0 weight%.

[Claim 8] The alkali-free glass according to Claim 1, characterized in that it is formed into a sheet by a downdraw process.

[Claim 9] The alkali-free glass according to Claim 1, characterized in that it has a composition, expressed in mass percentage, comprising SiO₂: 60–68%, Al₂O₃: 12–18%, B₂O₃: 7–12%, MgO: 0–1%, CaO: 4–10%, BaO: 0.3–2%, SrO: 0.1–2.7%, BaO+SrO: 0.4% or more and less than 3%, ZnO: 0–0.9%, MgO+CaO+BaO+SrO+ZnO: 5–12%, ZrO₂: 0–1%, TiO₂: 0–1%, P₂O₅: 0–1%.

[Claim 10] A glass substrate for displays, characterized in that it is made of an alkali-free glass having a composition, expressed in mass percentage, comprising SiO₂: 58–70%, Al₂O₃: 10–19%, B₂O₃: 6.5–15%, MgO: 0–2%, CaO: 3–12%, BaO: 0.1–5%, SrO: 0–4%, BaO+SrO: 0.1–6%, ZnO: 0–5%, MgO+CaO+BaO+SrO+ZnO: 5–15%, ZrO₂: 0–5%, TiO₂: 0–5%, P₂O₅: 0–5%, and being substantially free of alkali metal oxides, with a glass density of 2.45 g/cm³ or less, an average thermal expansion coefficient of 25–36×10⁻⁷/°C in the temperature range of 30–380°C, and a strain point of 640°C

or higher.

[Claim 11] The glass substrate for displays according to Claim 10, characterized in that it has a thickness of 0.6 mm or less.

[Claim 12] A liquid crystal display device, characterized in that it comprises the glass substrate according to Claim 10.

[Claim 13] A polycrystalline silicon TFT liquid crystal display device, characterized in that it comprises the glass substrate according to Claim 10.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The present invention relates to an alkali-free glass suitable for use as a glass substrate for flat display substrates such as liquid crystal displays and EL displays, as well as image sensors such as charge-coupled devices (CCD) and contact image sensors (CIS), and solar cells, and to a glass substrate for displays using the same.

[0002]

[Prior Art] Conventionally, glass substrates have been widely used as substrates for flat displays such as liquid crystal displays and EL displays.

[0003] In particular, electronic devices such as thin-film transistor active matrix liquid crystal displays (TFT-LCDs) are thin and consume low power, making them suitable for various applications, including car navigation systems, digital camera viewfinders, and, in recent years, computer monitors and televisions.

[0004] TFT-LCD panel manufacturers enhance productivity and reduce costs by fabricating multiple devices on a glass substrate (base plate) formed by a glass manufacturer, then dividing and cutting the substrate into individual devices to produce final products. In recent years, for applications such as TVs and computer monitors, larger devices have been required, necessitating large-area glass substrates, such as those measuring 1,000×1,200 mm, to accommodate multi-panel production.

[0005] Additionally, for portable devices such as cell phones and notebook computers, there is a demand for lighter equipment to enhance portability, which in turn requires lightweight glass substrates. To achieve lighter glass substrates, thinning the substrate is effective, and currently, the standard thickness for TFT-LCD glass substrates is approximately 0.7 mm, which is extremely thin.

[0006] However, such large and thin glass substrates exhibit significant deflection due to their own weight, posing a major issue in the manufacturing process.

[0007] Specifically, after being formed by a glass manufacturer, these glass substrates undergo processes such as cutting, annealing, inspection, and cleaning. During these processes, the glass substrates are loaded into and removed from cassettes equipped with multi-tiered shelves. These cassettes are designed to hold the glass substrates horizontally by placing their two or three edges on shelves formed on the inner two sides (left and right) or three sides (left, right, and back). However, large and thin glass substrates have a high degree of deflection, which causes

issues during handling: when inserting a glass substrate into the cassette's shelf, parts of the substrate may come into contact with the cassette or other glass substrates, leading to damage; and when removing the substrate from the shelf, it may swing significantly, resulting in instability. Similar issues arise at display manufacturers, where cassettes of the same type are used.

[0008] The amount of deflection in glass substrates due to their own weight is proportional to the glass density and inversely proportional to the Young's modulus. Therefore, to minimize the deflection of glass substrates, it is necessary to increase the specific Young's modulus, which is expressed as the ratio of Young's modulus to density. To achieve a high specific Young's modulus, a glass material with a high Young's modulus and low density is required. However, for glasses with the same specific Young's modulus, a glass with lower density allows for a thicker substrate at the same weight due to its lighter nature. Since the deflection of glass is inversely proportional to the square of the substrate thickness, the ability to increase thickness has a significant effect on reducing deflection. Lowering the glass density also greatly contributes to reducing the weight of the glass, so a lower density is preferable.

[0009] Generally, this type of alkali-free glass contains a relatively high amount of alkaline earth metal oxides. To reduce the density of the glass, it is effective to decrease the content of alkaline earth metal oxides; however, since these oxides are components that enhance the meltability of the glass, reducing their content leads to a decrease in meltability. When the meltability of glass decreases, internal defects such as bubbles and foreign matter are more likely to form in the glass. Bubbles and foreign matter in the glass obstruct light transmission, making them critical defects for glass substrates used in displays. To suppress such internal defects, the glass must be melted at high temperatures for extended periods.

[0010] However, high-temperature melting increases the burden on the glass melting furnace. For example, refractory materials such as alumina and zirconia used in the furnace are more severely eroded at higher temperatures, shortening the furnace's lifecycle. Additionally, the range of materials usable at high temperatures is limited, making all components more expensive. Furthermore, the running costs to maintain the furnace interior at consistently high temperatures are higher compared to glass that can be melted at lower temperatures. Thus, high-temperature melting is highly disadvantageous for glass production, and there is a demand for alkali-free glass that can be melted at lower temperatures.

[0011] Moreover, thermal shock resistance is a critical requirement for this type of glass substrate. Even if the edges of a glass substrate are chamfered, minute scratches or cracks remain. When tensile stress caused by heat concentrates on these scratches or cracks, the glass substrate may occasionally break. Glass breakage not only reduces the operational efficiency of the production line but also causes

fine glass particles generated during breakage to adhere to the glass substrate, significantly increasing the risk of defects such as disconnection or patterning failures.

[0012] In addition to increasing screen size and reducing weight, recent development trends for TFT-LCDs include performance enhancements such as higher resolution, faster response times, and higher aperture ratios. In particular, in recent years, the development of polycrystalline silicon TFT-LCDs (p-Si TFT-LCDs) has been actively pursued to achieve both high performance and lightweight liquid crystal displays. Conventionally, p-Si TFT-LCDs required extremely high manufacturing process temperatures of 800°C or more, limiting the use to quartz glass substrates. However, recent developments have reduced the manufacturing process temperature to 400–600°C, enabling the use of alkali-free glass substrates, similar to those used in the mass-produced amorphous silicon TFT-LCDs (a-Si TFT-LCDs).

[0013] Compared to the manufacturing process for a-Si TFT-LCDs, the p-Si TFT-LCD process involves more heat treatment steps, with the glass substrate subjected to repeated rapid heating and cooling, resulting in significantly greater thermal shock to the substrate. As previously mentioned, glass substrates are becoming larger, which not only increases the likelihood of temperature differences across the substrate but also raises the probability of minute scratches or cracks forming on the edges, thereby increasing the risk of substrate breakage during thermal processes. The most fundamental and effective solution to this issue is to reduce thermal stress caused by thermal expansion differences, necessitating glass with a low thermal expansion coefficient. Additionally, a large difference in thermal expansion between the glass substrate and thin-film transistor (TFT) materials can cause warping of the substrate, so it is also required that the glass has a thermal expansion coefficient close to that of TFT materials such as p-Si (approximately $30\text{--}33 \times 10^{-7}/^{\circ}\text{C}$).

[0014] Although the manufacturing process temperature for p-Si TFT-LCDs has recently decreased, it remains significantly higher than that for a-Si TFT-LCDs. If the heat resistance of the glass substrate is low, exposure to high temperatures of 400–600°C during the p-Si TFT-LCD manufacturing process can cause slight dimensional shrinkage known as thermal contraction, which may lead to misalignment of TFT pixel pitches and result in display defects. If the heat resistance of the glass substrate is even lower, deformation or warping of the substrate may occur. Furthermore, to prevent thermal contraction of the glass substrate during liquid crystal manufacturing processes such as film deposition, which could cause pattern misalignment, glass with excellent heat resistance is required.

[0015] Furthermore, on the surface of glass substrates for TFT-LCDs, transparent conductive films, insulating films, semiconductor films, metal films, and the like are deposited, and various circuits and patterns are formed through photolithographic etching (photoetching). During these deposition and photoetching processes, the glass substrate

undergoes various heat treatments and chemical treatments.

[0016] Consequently, if alkali metal oxides (Na_2O , K_2O , Li_2O) are present in the glass, alkali ions may diffuse into the deposited semiconductor material during heat treatment, leading to degradation of film properties. Therefore, it is required that the glass be substantially free of alkali metal oxides and possess chemical resistance to prevent deterioration from various acids, alkalis, and other chemicals used in the photoetching process.

[0017] Generally, the TFT array process consists of repeated cycles of deposition, resist pattern formation, etching, and resist stripping. As etching solutions, a variety of chemical liquids are used, including phosphoric acid-based solutions for etching Al and Mo-based films, aqua regia ($\text{HCl}+\text{HNO}_3$)-based solutions for etching ITO-based films, and buffered hydrofluoric acid (BHF) solutions for etching SiN_x and SiO_2 films. These solutions are managed in a circulating liquid flow system, rather than being discarded after a single use, to reduce costs.

[0018] If the chemical resistance of the glass substrate is low, various issues may arise during etching, such as reaction products between the chemical solution and the glass substrate clogging the filters in the circulating flow system, causing cloudiness on the glass surface due to non-uniform etching, or destabilizing the etching rate due to changes in the composition of the etching solution. In particular, hydrofluoric acid-based solutions, such as BHF, strongly erode glass substrates, making the aforementioned issues more likely to occur. Therefore, superior BHF resistance is particularly required.

[0019] Regarding the chemical resistance of glass substrates, it is important not only to minimize erosion but also to prevent changes in appearance. In other words, low erosion by chemical solutions is highly significant in preventing contamination of the solution and clogging of filters by reaction products during the process. Additionally, ensuring that the glass does not exhibit changes in appearance, such as cloudiness or surface roughness, after chemical treatment is an essential property for display substrates where light transmittance is critical.

[0020] The evaluation results for erosion and appearance changes, particularly for BHF resistance, do not always align. For instance, even glasses with the same degree of erosion may or may not exhibit appearance changes after chemical treatment, depending on their composition.

[0021] Furthermore, glass substrates for TFT-LCDs are primarily formed using the downdraw method or the float method. Examples of the downdraw method include the slot downdraw method and the overflow downdraw method. Glass substrates formed by the downdraw method do not require polishing, offering the advantage of cost reduction. However, when forming glass substrates using the downdraw method, the glass is prone to devitrification, necessitating glass with excellent devitrification resistance.

[0022]

[Problems to be Solved by the Invention] Currently, glass

substrates for TFT-LCDs, such as Corning's 1737 glass and Nippon Electric Glass Co., Ltd.'s OA-10 glass, are commercially available. These glasses have a strain point of approximately 650°C , providing excellent heat resistance. However, their high thermal expansion coefficients and densities make them insufficient in thermal shock resistance, particularly when used as glass substrates for P-Si TFTs. Additionally, their high weight makes it difficult to achieve large-sized and thin substrates.

[0023] The objective of the present invention is to provide an alkali-free glass that satisfies the properties required for TFT-LCD glass substrates, is lightweight, exhibits low deflection, and has a thermal expansion coefficient of $25\text{--}36 \times 10^{-7}/^\circ\text{C}$, making it suitable for use as a glass substrate for P-Si TFT-LCDs.

[0024]

[Means for Solving the Problem] Through repeated experiments, the inventors have identified a glass composition that satisfies the various properties required for glass substrates used in TFT-LCDs and offers excellent productivity, which is proposed as the present invention.

[0025] Specifically, the alkali-free glass of the present invention has a composition, expressed in mass percentage, comprising SiO_2 : 58–70%, Al_2O_3 : 10–19%, B_2O_3 : 6.5–15%, MgO : 0–2%, CaO : 3–12%, BaO : 0.1–5%, SrO : 0–4%, $\text{BaO}+\text{SrO}$: 0.1–6%, ZnO : 0–5%, $\text{MgO}+\text{CaO}+\text{BaO}+\text{SrO}+\text{ZnO}$: 5–15%, ZrO_2 : 0–5%, TiO_2 : 0–5%, P_2O_5 : 0–5%, is substantially free of alkali metal oxides, and is characterized by a density of 2.45 g/cm^3 or less, an average thermal expansion coefficient of $25\text{--}36 \times 10^{-7}/^\circ\text{C}$ in the temperature range of $30\text{--}380^\circ\text{C}$, and a strain point of 640°C or higher.

[0026] Additionally, the alkali-free glass of the present invention preferably has a composition, expressed in mass percentage, comprising SiO_2 : 60–68%, Al_2O_3 : 12–18%, B_2O_3 : 7–12%, MgO : 0–1%, CaO : 4–12%, BaO : 0.3–2%, SrO : 0.1–2.7%, $\text{BaO}+\text{SrO}$: 0.4% or more and less than 3%, ZnO : 0–0.9%, $\text{MgO}+\text{CaO}+\text{BaO}+\text{SrO}+\text{ZnO}$: 5–12%, ZrO_2 : 0–1%, TiO_2 : 0–1%, P_2O_5 : 0–1%.

[0027] Furthermore, the glass substrate for displays of the present invention is made of an alkali-free glass having a composition, expressed in mass percentage, comprising SiO_2 : 58–70%, Al_2O_3 : 10–19%, B_2O_3 : 6.5–15%, MgO : 0–2%, CaO : 3–12%, BaO : 0.1–5%, SrO : 0–4%, $\text{BaO}+\text{SrO}$: 0.1–6%, ZnO : 0–5%, $\text{MgO}+\text{CaO}+\text{BaO}+\text{SrO}+\text{ZnO}$: 5–15%, ZrO_2 : 0–5%, TiO_2 : 0–5%, P_2O_5 : 0–5%, is substantially free of alkali metal oxides, and is characterized by a density of 2.45 g/cm^3 or less, an average thermal expansion coefficient of $25\text{--}36 \times 10^{-7}/^\circ\text{C}$ in the temperature range of $30\text{--}380^\circ\text{C}$, and a strain point of 640°C or higher.

[0028]

[Effect] The alkali-free glass of the present invention has a composition specified in consideration of strain point, density, thermal expansion coefficient, chemical resistance, specific Young's modulus, meltability, and formability, and is characterized by a density of 2.45 g/cm^3 or less, an average thermal expansion coefficient of $25\text{--}36 \times 10^{-7}/^\circ\text{C}$ in the

temperature range of 30–380°C, and a strain point of 640°C or higher, resulting in excellent thermal shock resistance, compatibility with the thermal expansion coefficient of TFT materials to prevent warping, reduced weight, minimized deflection, and low thermal contraction.

[0029] In the present invention, the preferred density range is 2.40 g/cm³ or less, the preferred average thermal expansion coefficient range is 28–35×10⁻⁷/°C, and the preferred strain point range is 650°C or higher, with a more preferred range of 660°C or higher.

[0030] Additionally, the alkali-free glass of the present invention has a liquidus temperature of 1,150°C or lower (preferably 1,130°C or lower, more preferably 1,100°C or lower) and a viscosity at the liquidus temperature of 10^{5.4} dPa·s or higher (preferably 10^{6.0} dPa·s or higher), enabling formation into sheets by the downdraw method without devitrification and allowing the omission of polishing processes to reduce production costs. Furthermore, when treated with a 10% HCl aqueous solution at 80°C for 24 hours, the erosion is 10 μm or less, and when treated with a 10% HCl aqueous solution at 80°C for 3 hours, no cloudiness or surface roughness is observed by visual inspection; additionally, when treated with a 130BHF solution at 20°C for 30 minutes, the erosion is 0.8 μm or less, and when treated with a 63BHF solution at 20°C for 30 minutes, no cloudiness or surface roughness is observed by visual inspection, demonstrating excellent chemical resistance. Moreover, with a specific Young's modulus of 27.5 GPa/g·cm⁻³ or higher (preferably 29.0 GPa/g·cm⁻³ or higher), the deflection of the glass substrate can be minimized. Furthermore, since the temperature of the glass melt at a viscosity of 10^{2.5} dPa·s is 1,650°C or lower, the meltability is also excellent.

[0031] Additionally, the glass substrate for displays of the present invention, with its low density and high specific Young's modulus, exhibits minimal reduction in workability even when the thickness is 0.6 mm or less (preferably 0.5 mm or less). In other words, even when the thickness is reduced from 0.7 mm to 0.6 mm or less, the deflection amount is smaller compared to conventional glass substrates, making it easier to prevent damage during the loading and unloading of the glass substrate into and from the cassette shelves.

[0032] The reasons for limiting each component of the alkali-free glass of the present invention are explained below.

[0033] The SiO₂ content in the present invention is 58–70%. If it is less than 58%, chemical resistance, particularly acid resistance, deteriorates, and achieving low density becomes difficult. If it exceeds 70%, the high-temperature viscosity increases, impairing meltability, and defects such as devitrification foreign matter (cristobalite) are more likely to occur in the glass. The preferred SiO₂ content is 60% or more (more preferably 62% or more) and 68% or less (more preferably 66% or less).

[0034] The Al₂O₃ content is 10–19%. If it is less than 10%, it becomes difficult to achieve a strain point of 640°C

or higher. Additionally, Al₂O₃ enhances the Young's modulus of the glass and increases the specific Young's modulus, but if it is less than 10%, the Young's modulus decreases. If it exceeds 19%, the liquidus temperature increases, reducing devitrification resistance. The preferred Al₂O₃ content is 12% or more (more preferably 14.5% or more) and 18.0% or less.

[0035] It should be noted that the alkali-free glass of the present invention tends to precipitate mullite or anorthite as devitrification crystals alongside cristobalite. The degree of precipitation of these devitrification crystals is significantly influenced by the molar ratio of the total moles of alkaline earth metal oxides excluding MgO to the moles of Al₂O₃, i.e., (CaO+BaO+SrO)/Al₂O₃. If this molar ratio is 0.8 or less, the devitrification tendency increases, reducing formability, which is undesirable. Conversely, if it is 1.5 or more, the density increases, which is also undesirable. A more preferable range for this molar ratio is 9-1.2.

[0036] B₂O₃ acts as a flux, lowering viscosity and improving meltability. If B₂O₃ is less than 6.5%, its function as a flux is insufficient, and resistance to buffered hydrofluoric acid deteriorates. If B₂O₃ exceeds 15%, the strain point of the glass decreases, reducing heat resistance and deteriorating acid resistance. Furthermore, the Young's modulus decreases, leading to a reduction in specific Young's modulus. The preferred B₂O₃ content is 7% or more (more preferably 8.6% or more) and 14% or less (more preferably 12% or less).

[0037] MgO lowers high-temperature viscosity and improves the meltability of the glass without reducing the strain point. Among alkaline earth metal oxides, it has the most significant effect on reducing density. However, if contained in large amounts, the liquidus temperature increases, reducing devitrification resistance. Additionally, MgO reacts with buffered hydrofluoric acid to form reaction products that may adhere to the surface of elements on the glass substrate or cause cloudiness by adhering to the substrate, necessitating restrictions on its content. Therefore, the MgO content is 0–2%, preferably 0–1%, more preferably 0–0.5%, and it is even more desirable for the glass to be substantially free of MgO.

[0038] CaO, like MgO, is a component that lowers high-temperature viscosity and significantly improves the meltability of the glass without reducing the strain point, with a content of 3–12%. This type of alkali-free glass substrate is generally difficult to melt, and enhancing its meltability is crucial for supplying high-quality glass substrates in large quantities at low cost. In the glass composition system of the present invention, reducing SiO₂ is the most effective way to enhance meltability; however, decreasing the SiO₂ content significantly impairs acid resistance and increases the glass's density and thermal expansion coefficient, which is undesirable. Therefore, in the present invention, CaO is included at 3% or more to improve the meltability of the glass. If CaO is less than 3%, achieving a molar ratio of (CaO+BaO+SrO)/Al₂O₃ in the range of 0.8–1.5 would

require incorporating higher amounts of BaO or SrO. However, including large amounts of BaO or SrO significantly increases the density, which is undesirable. On the other hand, if CaO exceeds 12%, the glass's resistance to buffered hydrofluoric acid deteriorates, making the glass substrate surface more susceptible to erosion, and reaction products may adhere to the surface, causing cloudiness. Additionally, the thermal expansion coefficient becomes excessively high, which is undesirable. The preferred CaO content is 4% or more (more preferably 5% or more) and 10% or less (more preferably 9% or less).

[0039] BaO and SrO are components that improve the chemical resistance and devitrification resistance of the glass, but if contained in large amounts, they increase the glass's density and thermal expansion coefficient. Therefore, their respective contents must be restricted to 0.1–5% for BaO and 0–4% for SrO. Particularly when reducing BaO and SrO to achieve lower density, if the contents of these two components become extremely imbalanced, the effect of improving BHF resistance diminishes. Thus, it is desirable to include both components such that the mass ratio (BaO+SrO)/BaO satisfies the range of 1.1–10 (preferably 1.2–5). The preferred BaO content is 0.3% or more (more preferably 0.5% or more) and 2% or less (more preferably 1% or less), and the preferred SrO content is 0.1–2.7%, more preferably 0.3–1.5%.

[0040] Additionally, BaO and SrO are components that particularly enhance BHF resistance. Therefore, to improve BHF resistance, it is necessary to include these components in a combined amount of 0.1% or more (preferably 0.3% or more, more preferably 0.5% or more). However, as mentioned earlier, if BaO and SrO are included in excessive amounts, the density and thermal expansion coefficient of the glass increase, necessitating their combined content to be limited to 6% or less. Within this range, from the perspective of enhancing BHF resistance, it is desirable to include as much BaO and SrO as possible, while from the perspective of reducing density and thermal expansion coefficient, it is preferable to include as little as possible.

[0041] ZnO is a component that improves the buffered hydrofluoric acid resistance and meltability of the glass substrate, but if included in large amounts, it makes the glass prone to devitrification, lowers the strain point, and increases density, which is undesirable. Therefore, its content is 0–5%, preferably 3% or less, more preferably 0.9% or less, and most preferably 0.5% or less.

[0042] Incorporating a combination of MgO, CaO, BaO, SrO, and ZnO significantly lowers the liquidus temperature of the glass, making it less likely to form crystalline foreign matter, thereby improving the meltability and formability of the glass. However, if their combined content is less than 5%, their function as a flux is insufficient, leading to poor meltability, and the thermal expansion coefficient becomes too low, reducing compatibility with TFT materials. Conversely, if their combined content exceeds 15%, the density increases, hindering the lightweighting of the glass

substrate, and the specific Young's modulus decreases, which is undesirable. The preferred range for the combined content of these components is 5–12%, with a more preferred range of 5–10%.

[0043] ZrO₂ is a component that improves the chemical resistance, particularly acid resistance, and enhances the Young's modulus of the glass, but if it exceeds 5%, the liquidus temperature rises, and zircon devitrification foreign matter is likely to form, which is undesirable. The preferred range for ZrO₂ is 0–3%, more preferably 0–1%.

[0044] TiO₂ is a component that improves the chemical resistance, particularly acid resistance, and lowers high-temperature viscosity to enhance meltability, but if included in large amounts, it causes coloration in the glass, reducing its transmittance, which is undesirable for glass substrates used in displays. Therefore, TiO₂ should be restricted to 0–5%, preferably 0–3%, and more preferably 0–1%.

[0045] P₂O₅ is a component that improves the devitrification resistance of the glass, but if included in large amounts, it causes phase separation and opacification in the glass, as well as significantly deteriorating acid resistance, which is undesirable. Therefore, P₂O₅ should be restricted to 0–5%, preferably 0–3%, and more preferably 0–1%.

[0046] In addition to the above components, the present invention may include up to about 5% of Y₂O₃, Nb₂O₃, and La₂O₃. These components enhance the strain point and Young's modulus, but including them in large amounts increases the density, which is undesirable.

[0047] Furthermore, as long as the glass properties are not impaired, the glass of the present invention may contain up to 5% of clarificants such as As₂O₃, Sb₂O₃, Sb₂O₅, F₂, Cl₂, SO₃, C, or metal powders like Al and Si. Additionally, CeO₂, SnO₂, Fe₂O₃, and the like can also be included as clarificants up to 5%.

[0048] Conventionally, when melting alkali-free glass as in the present invention, As₂O₃, which acts as a clarificant at high temperatures, has been used. However, in recent years, due to environmental considerations, the use of environmentally hazardous substances like As₂O₃ has become less feasible. SnO₂, like As₂O₃, has clarifying capabilities at high temperatures and is highly effective as a clarificant for melting the alkali-free glass of the present invention. However, if SnO₂ is included in large amounts, it causes devitrification, so its content is restricted to 5% or less, preferably 2% or less.

[0049] Additionally, Cl promotes the melting of alkali-free glass, and its addition enables melting at lower temperatures, enhancing the effectiveness of clarificants, reducing glass melting costs, and extending the lifespan of manufacturing equipment. However, excessive inclusion of Cl lowers the strain point of the glass, so its content is preferably restricted to 3% or less. As raw materials for the Cl component, chlorides of alkaline earth metal oxides such as barium chloride or raw materials like aluminum chloride can be used.

[0050] Furthermore, Sb₂O₃ and Sb₂O₅ are also effective

as clarificants for the alkali-free glass of the present invention, but since alkali-free glass has a high melting temperature, their effectiveness as clarificants is lower compared to As_2O_3 . Therefore, when using Sb_2O_3 or Sb_2O_5 , it is desirable to either increase their amounts or combine them with components like Cl that promote meltability to lower the melting temperature. However, including Sb_2O_3 or Sb_2O_5 at 5% or more leads to an increase in density, so their content is preferably limited to 2% or less, more preferably 1.5% or less.

[0051] In the present invention, when As_2O_3 is not used as a clarificant, it is preferable to include 0.5–3.0% of one or more components selected from the group consisting of Sb_2O_3 , Sb_2O_5 , SnO_2 , and Cl. Most preferably, the glass contains $\text{Sb}_2\text{O}_3+\text{Sb}_2\text{O}_5$ at 0.05–2.0%, SnO_2 at 0.01–1.0%, and Cl at 0.005–1.0% .

[0052]

[Examples] The present invention is described in detail below based on examples.

[0053] Tables 1–17 show the glass compositions of the examples of the present invention (Samples No. 1–46) and comparative example glasses (Samples No. 47–49). Note that Sample No. 49 represents Corning's 1737 glass.

[0054]

[Table 1]

		Sample No. 1		Sample No. 2		Sample No. 3	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		61.2	67.5	62.1	68.4	61.7	67.9
Al ₂ O ₃		16.8	10.9	16.3	10.6	16.3	10.6
B ₂ O ₃		11.8	11.3	11.4	10.8	11.8	11.3
MgO		-	-	-	-	-	-
CaO		7.9	9.3	7.9	9.3	7.9	9.3
SrO		0.5	0.3	0.5	0.3	0.5	0.3
BaO		0.5	0.2	0.5	0.2	0.5	0.2
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		-	-	-	-	-	-
Sb ₂ O ₃		1.0	0.2	1.0	0.2	1.0	0.2
ZrO ₂		0.3	0.2	0.3	0.2	0.3	0.2
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		2		2		2	
Density (g/cm ³)		2.384		2.383		2.382	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		33		33	
Viscosity	Strain point (°C)	667		668		665	
	Annealing point (°C)	724		725		722	
	Softening point (°C)	973		977		971	
	10 ^{4.0} (°C)	1301		1316		1305	
	10 ^{3.0} (°C)	1467		1485		1474	
	10 ^{2.5} (°C)	1573		1594		1581	
Young's modulus		69		69		69	
Specific Young's modulus		29.1		29.1		28.8	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	7.3		6.0		7.2	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1123		1092		1094	
Liquidus viscosity		10 ^{5.6}		10 ^{6.1}		10 ^{5.9}	

[0055]

[Table 2]

		Sample No. 4		Sample No. 5		Sample No. 6	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		61.2	67.4	61.2	67.2	61.7	68.2
Al ₂ O ₃		16.8	10.9	16.8	10.9	17.0	11.1
B ₂ O ₃		11.8	11.3	11.8	11.2	10.5	10.0
MgO		0.5	0.8	1.0	1.6	-	-
CaO		7.4	8.7	6.9	9.3	8.0	9.5
SrO		0.5	0.3	0.5	0.3	1.0	0.6
BaO		0.5	0.2	0.5	0.2	0.5	0.2
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		-	-	-	-	-	-
Sb ₂ O ₃		1.0	0.2	1.0	0.2	1.0	0.2
ZrO ₂		0.3	0.2	0.3	0.2	0.3	0.2
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		2		2		3	
Density (g/cm ³)		2.382		2.379		2.400	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		32		34	
Viscosity	Strain point (°C)	669		670		674	
	Annealing point (°C)	724		724		731	
	Softening point (°C)	973		973		984	
	10 ^{4.0} (°C)	1301		1301		1322	
	10 ^{3.0} (°C)	1467		1467		1488	
	10 ^{2.5} (°C)	1573		1573		1597	
Young's modulus		70		70		71	
Specific Young's modulus		29.3		29.5		29.4	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	7.3		7.3		4.6	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1128		1146		1094	
Liquidus viscosity		10 ^{5.6}		10 ^{5.4}		10 ^{6.1}	

[0056]

[Table 3]

		Sample No. 7		Sample No. 8		Sample No. 9	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		63.5	67.3	61.8	68.3	62.8	69.2
Al ₂ O ₃		16.5	10.6	17.0	11.1	16.5	10.7
B ₂ O ₃		10.5	9.9	10.5	10.0	10.0	9.5
MgO		-	-	-	-	-	-
CaO		8.0	9.4	8.0	9.5	8.0	9.5
SrO		1.0	0.6	0.5	0.3	0.5	0.3
BaO		0.5	0.2	0.6	0.3	0.6	0.3
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		-	-	0.3	0.1	0.3	0.1
Sb ₂ O ₃		-	-	1.0	0.2	1.0	0.2
ZrO ₂		-	-	0.3	0.2	0.3	0.2
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		3		1.8		1.8	
Density (g/cm ³)		2.375		2.395		2.393	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		33		33	
Viscosity	Strain point (°C)	675		675		676	
	Annealing point (°C)	734		733		734	
	Softening point (°C)	991		989		993	
	10 ^{4.0} (°C)	1353		1332		1347	
	10 ^{3.0} (°C)	1527		1499		1517	
	10 ^{2.5} (°C)	1641		1610		1631	
Young's modulus		69		70		70	
Specific Young's modulus		29.2		29.4		29.2	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	4.6		4.6		4.2	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1065		1118		1085	
Liquidus viscosity		10 ^{6.6}		10 ^{5.9}		10 ^{6.4}	

[0057]

[Table 4]

		Sample No. 10		Sample No. 11		Sample No. 12	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		61.8	68.8	60.8	67.7	61.8	68.7
Al ₂ O ₃		17.0	11.2	17.0	11.1	17.0	11.1
B ₂ O ₃		10.5	10.1	10.5	10.1	9.5	9.1
MgO		-	-	-	-	-	-
CaO		7.0	8.4	8.0	9.5	8.0	9.5
SrO		0.5	0.3	0.5	0.3	0.5	0.3
BaO		0.6	0.3	0.6	0.3	0.6	0.3
ZnO		-	-	-	-	-	-
P ₂ O ₅		1.0	0.5	1.0	0.5	1.0	0.5
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		0.3	0.1	0.3	0.1	0.3	0.1
Sb ₂ O ₃		1.0	0.2	1.0	0.2	1.0	0.2
ZrO ₂		0.3	0.2	0.3	0.2	0.3	0.2
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		1.8		1.8		1.8	
Density (g/cm ³)		2.374		2.395		2.397	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		31		33		33	
Viscosity	Strain point (°C)	680		675		681	
	Annealing point (°C)	739		733		739	
	Softening point (°C)	1007		989		1000	
	10 ^{4.0} (°C)	1362		1332		1354	
	10 ^{3.0} (°C)	1534		1499		1522	
	10 ^{2.5} (°C)	1647		1610		1636	
Young's modulus		69		70		71	
Specific Young's modulus		29.2		29.4		29.6	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	4.6		4.6		3.5	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1124		1118		1122	
Liquidus viscosity		10 ^{6.1}		10 ^{5.9}		10 ^{6.0}	

[0058]

[Table 5]

		Sample No. 13		Sample No. 14		Sample No. 15	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		61.8	68.2	61.8	68.0	63.0	69.0
Al ₂ O ₃		17.0	11.1	17.0	11.0	17.0	11.0
B ₂ O ₃		10.5	10.0	10.5	10.0	10.0	9.5
MgO		0.5	0.8	1.0	1.6	-	-
CaO		7.5	8.9	7.0	8.3	8.0	9.4
SrO		0.5	0.3	0.5	0.3	1.3	0.8
BaO		0.6	0.3	0.6	0.3	0.7	0.3
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		0.3	0.1	0.3	0.1	-	-
Sb ₂ O ₃		1.0	0.2	1.0	0.2	-	-
ZrO ₂		0.3	0.2	0.3	0.2	-	-
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		1.8		1.8		2.9	
Density(g/cm ³)		2.392		2.389		2.390	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		32		32		34	
Viscosity	Strain point (°C)	677		678		678	
	Annealing point (°C)	733		733		737	
	Softening point (°C)	989		989		993	
	10 ^{4.0} (°C)	1332		1332		1349	
	10 ^{3.0} (°C)	1499		1499		1520	
	10 ^{2.5} (°C)	1610		1610		1632	
Young's modulus		71		71		71	
Specific Young's modulus		29.5		29.7		29.6	
BHF resistance	Corrosion (μm)	0.7		0.8		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	4.6		4.6		3.0	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1133		1148		1066	
Liquidus viscosity		10 ^{5.7}		10 ^{5.5}		10 ^{6.6}	

[0059]

[Table 6]

		Sample No. 16		Sample No. 17		Sample No. 18	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		63.1	69.5	62.6	69.1	62.5	69.1
Al ₂ O ₃		17.9	11.6	17.9	11.7	17.5	11.4
B ₂ O ₃		9.5	9.0	9.5	9.1	9.5	9.1
MgO		-	-	-	-	-	-
CaO		7.8	9.2	7.8	9.2	7.8	9.3
SrO		0.2	0.1	0.5	0.3	0.5	0.3
BaO		0.8	0.4	1.0	0.4	1.5	0.7
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		-	-	-	-	-	-
Sb ₂ O ₃		0.7	0.2	0.7	0.2	0.7	0.2
ZrO ₂		-	-	-	-	-	-
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		1.3		1.5		1.3	
Density (g/cm ³)		2.381		2.392		2.402	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		32		33		33	
Viscosity	Strain point (°C)	686		685		681	
	Annealing point (°C)	745		743		739	
	Softening point (°C)	1011		1006		1001	
	10 ^{4.0} (°C)	1368		1357		1350	
	10 ^{3.0} (°C)	1537		1526		1522	
	10 ^{2.5} (°C)	1650		1637		1633	
Young's modulus		71		72		71	
Specific Young's modulus		29.9		29.9		29.7	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	3.6		3.6		3.7	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1146		1149		1123	
Liquidus viscosity		10 ^{5.9}		10 ^{5.8}		10 ^{6.0}	

[0060]

[Table 7]

		Sample No. 19		Sample No. 20		Sample No. 21	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		62.9	69.2	63.0	69.4	62.6	69.2
Al ₂ O ₃		17.0	11.0	17.5	11.4	16.0	10.4
B ₂ O ₃		9.9	9.4	9.9	9.4	10.3	9.8
MgO		-	-	-	-	-	-
CaO		7.8	9.2	7.8	9.2	7.8	9.2
SrO		1.0	0.6	0.2	0.1	1.0	0.6
BaO		1.0	0.4	0.4	0.2	0.6	0.3
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		-	-	-	-	-	-
Sb ₂ O ₃		0.3	0.1	1.0	0.2	1.5	0.3
ZrO ₂		0.1	0.1	0.2	0.1	0.2	0.1
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		2		1.5		2.7	
Density (g/cm ³)		2.393		2.377		2.399	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		32		33	
Viscosity	Strain point (°C)	679		683		670	
	Annealing point (°C)	737		742		727	
	Softening point (°C)	996		1006		982	
	10 ^{4.0} (°C)	1350		1360		1331	
	10 ^{3.0} (°C)	1522		1528		1503	
	10 ^{2.5} (°C)	1634		1641		1651	
Young's modulus		71		71		69	
Specific Young's modulus		29.6		29.7		28.8	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	3.8		3.8		4.5	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1092		1149		1058	
Liquidus viscosity		10 ^{6.3}		10 ^{5.8}		10 ^{6.6}	

[0061]

[Table 8]

		Sample No. 22		Sample No. 23		Sample No. 24	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		63.8	69.8	63.7	69.9	65.3	70.7
Al ₂ O ₃		15.1	9.7	15.1	9.8	14.6	9.3
B ₂ O ₃		10.3	9.7	10.3	9.8	9.4	8.8
MgO		-	-	-	-	-	-
CaO		7.8	9.2	7.8	9.2	9.0	10.5
SrO		1.1	0.7	1.1	0.7	0.5	0.3
BaO		0.7	0.3	0.7	0.3	0.5	0.2
ZnO		0.4	0.3	-	-	-	-
P ₂ O ₅		-	-	0.5	0.2	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		0.1	<0.05	0.1	<0.05	-	-
Sb ₂ O ₃		0.7	0.2	0.7	0.2	0.7	0.2
ZrO ₂		-	-	-	-	-	-
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		2.6		2.6		2	
Density (g/cm ³)		2.393		2.384		2.389	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		33		34	
Viscosity	Strain point (°C)	666		668		667	
	Annealing point (°C)	723		726		726	
	Softening point (°C)	978		984		980	
	10 ^{4.0} (°C)	1342		1354		1359	
	10 ^{3.0} (°C)	1519		1534		1539	
	10 ^{2.5} (°C)	1634		1650		1650	
Young's modulus		68		68		68	
Specific Young's modulus		28.3		28.4		28.5	
BHF resistance	Corrosion (μm)	0.5		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	4.5		4.5		3.4	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1055		1055		1054	
Liquidus viscosity		10 ^{6.6}		10 ^{6.7}		10 ^{6.7}	

[0062]

[Table 9]

		Sample No. 25		Sample No. 26		Sample No. 27	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		63.3	69.5	64.0	69.6	63.6	69.9
Al ₂ O ₃		15.0	9.7	15.0	9.6	15.8	10.2
B ₂ O ₃		12.0	11.4	10.0	9.4	10.3	9.7
MgO		-	-	-	-	-	-
CaO		7.0	8.2	10.0	11.6	7.6	9.0
SrO		1.0	0.7	0.5	0.3	1.0	0.6
BaO		1.0	0.4	0.5	0.2	0.5	0.2
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		-	-	-	-	0.1	<0.05
Sb ₂ O ₃		0.7	0.2	-	-	1.0	0.2
ZrO ₂		-	-	-	-	0.1	0.1
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		2		2		3	
Density (g/cm ³)		2.365		2.399		2.386	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		32		36		33	
Viscosity	Strain point (°C)	661		664		671	
	Annealing point (°C)	720		720		730	
	Softening point (°C)	977		961		988	
	10 ^{4.0} (°C)	1339		1326		1346	
	10 ^{3.0} (°C)	1521		1502		1520	
	10 ^{2.5} (°C)	1635		1619		1634	
Young's modulus		66		69		69	
Specific Young's modulus		27.9		28.7		28.8	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	7.1		4.1		4.5	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1060		1050		1102	
Liquidus viscosity		10 ^{6.5}		10 ^{6.4}		10 ^{6.1}	

[0063]

[Table 10]

		Sample No. 28		Sample No. 29		Sample No. 30	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		63.3	69.7	63.1	69.5	63.1	69.4
Al ₂ O ₃		16.1	10.4	16.3	10.6	16.1	10.4
B ₂ O ₃		10.3	9.8	10.3	9.8	10.3	9.7
MgO		-	-	-	-	-	-
CaO		7.6	9.0	7.6	9.0	7.8	9.2
SrO		1.0	0.6	1.0	0.6	0.5	0.3
BaO		0.5	0.2	0.5	0.2	0.5	0.2
ZnO		-	-	-	-	0.5	0.4
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		0.1	<0.05	0.1	<0.05	0.1	<0.05
Sb ₂ O ₃		1.0	0.2	1.0	0.2	1.0	0.2
ZrO ₂		0.1	0.1	0.1	0.1	0.1	0.1
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		3		3		2	
Density (g/cm ³)		2.388		2.389		2.392	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		33		33	
Viscosity	Strain point (°C)	673		674		671	
	Annealing point (°C)	731		732		728	
	Softening point (°C)	989		990		984	
	10 ^{4.0} (°C)	1344		1342		1334	
	10 ^{3.0} (°C)	1516		1514		1504	
	10 ^{2.5} (°C)	1629		1626		1615	
Young's modulus		69		69		69	
Specific Young's modulus		28.9		29.0		28.8	
BHF resistance	Corrosion (μm)	0.6		0.6		0.5	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	4.5		4.5		4.5	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1103		1104		1091	
Liquidus viscosity		10 ^{6.1}		10 ^{6.3}		10 ^{6.2}	

[0064]

[Table 11]

		Sample No. 31		Sample No. 32		Sample No. 33	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		63.4	69.6	62.9	69.2	63.8	69.9
Al ₂ O ₃		15.8	10.2	16.3	10.6	15.8	10.2
B ₂ O ₃		10.3	9.7	10.3	9.8	10.3	9.7
MgO		-	-	-	-	-	-
CaO		7.8	9.2	7.8	9.2	7.9	9.3
SrO		0.5	0.3	0.5	0.3	0.5	0.3
BaO		0.5	0.2	0.5	0.2	0.5	0.2
ZnO		0.5	0.4	0.5	0.4	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		0.1	<0.05	0.1	<0.05	0.1	<0.05
Sb ₂ O ₃		1.0	0.2	1.0	0.2	1.0	0.2
ZrO ₂		0.1	0.1	0.1	0.1	0.1	0.1
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		2		2		2	
Density (g/cm ³)		2.390		2.393		2.381	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		33		33	
Viscosity	Strain point (°C)	670		672		671	
	Annealing point (°C)	726		726		730	
	Softening point (°C)	983		984		988	
	10 ^{4.0} (°C)	1336		1332		1349	
	10 ^{3.0} (°C)	1507		1501		1523	
	10 ^{2.5} (°C)	1620		1611		1638	
Young's modulus		68		69		69	
Specific Young's modulus		28.7		28.9		28.8	
BHF resistance	Corrosion (μm)	0.5		0.5		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	4.5		4.5		4.5	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1088		1112		1063	
Liquidus viscosity		10 ^{6.2}		10 ^{6.0}		10 ^{6.6}	

[0065]

[Table 12]

		Sample No. 34		Sample No. 35		Sample No. 36	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		63.5	69.7	63.3	69.6	63.2	69.5
Al ₂ O ₃		16.1	10.4	16.3	10.6	15.9	10.3
B ₂ O ₃		10.3	9.7	10.3	9.7	10.4	9.9
MgO		-	-	-	-	-	-
CaO		7.9	9.3	7.9	9.3	7.6	9.0
SrO		0.5	0.3	0.5	0.3	1.0	0.7
BaO		0.5	0.2	0.5	0.2	0.5	0.2
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	0.7	0.2
SnO ₂		0.1	<0.05	0.1	<0.05	-	-
Sb ₂ O ₃		1.0	0.2	1.0	0.2	0.5	0.1
ZrO ₂		0.1	0.1	0.1	0.1	0.1	0.1
Cl		-	-	-	-	0.1	0.2
(BaO + SrO)/BaO		2		2		3	
Density (g/cm ³)		2.382		2.384		2.382	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		33		33	
Viscosity	Strain point (°C)	673		674		676	
	Annealing point (°C)	731		732		735	
	Softening point (°C)	989		990		987	
	10 ^{4.0} (°C)	1346		1345		1324	
	10 ^{3.0} (°C)	1519		1516		1498	
	10 ^{2.5} (°C)	1633		1630		1612	
Young's modulus		69		69		70	
Specific Young's modulus		29.0		29.0		29.4	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	4.5		4.5		2.1	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1082		1090		1105	
Liquidus viscosity		10 ^{6.4}		10 ^{6.3}		10 ^{6.0}	

[0066]

[Table 13]

		Sample No. 37		Sample No. 38		Sample No. 39	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		63.3	69.5	63.1	69.5	63.0	69.4
Al ₂ O ₃		15.9	10.3	15.9	10.3	15.9	10.3
B ₂ O ₃		10.4	9.9	10.4	9.9	10.4	9.9
MgO		-	-	-	-	-	-
CaO		7.6	9.0	7.6	9.0	7.6	9.0
SrO		1.0	0.7	0.5	0.3	0.5	0.3
BaO		0.5	0.2	1.2	0.5	1.2	0.5
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	0.7	0.2
SnO ₂		0.1	<0.05	0.1	<0.05	-	-
Sb ₂ O ₃		1.0	0.2	1.0	0.2	0.5	0.1
ZrO ₂		0.1	0.1	0.1	0.1	0.1	0.1
Cl		0.1	0.2	0.1	0.2	0.1	0.2
(BaO + SrO)/BaO		3		1.4		1.4	
Density (g/cm ³)		2.387		2.388		2.384	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		33		33		33	
Viscosity	Strain point (°C)	676		671		672	
	Annealing point (°C)	732		729		729	
	Softening point (°C)	987		989		989	
	10 ^{4.0} (°C)	1327		1348		1342	
	10 ^{3.0} (°C)	1501		1525		1516	
	10 ^{2.5} (°C)	1612		1639		1628	
Young's modulus		71		69		69	
Specific Young's modulus		29.7		28.7		28.8	
BHF resistance	Corrosion (μm)	0.6		0.6		0.6	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	2.3		2.1		2.2	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1101		1099		1101	
Liquidus viscosity		10 ^{6.1}		10 ^{6.2}		10 ^{6.1}	

[0067]

[Table 14]

		Sample No. 40		Sample No. 41		Sample No. 42	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		61.2	68.6	60.2	68.0	61.1	68.9
Al ₂ O ₃		15.8	10.5	15.8	10.5	15.8	10.5
B ₂ O ₃		11.8	11.4	11.8	11.5	10.9	10.6
MgO		-	-	-	-	-	-
CaO		5.9	7.1	5.9	7.1	5.9	7.1
SrO		1.0	0.6	1.0	0.7	1.0	0.7
BaO		3.0	1.3	3.0	1.3	3.0	1.3
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	1.0	0.5	1.0	0.5
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		-	-	-	-	-	-
Sb ₂ O ₃		1.0	0.2	1.0	0.2	1.0	0.2
ZrO ₂		0.3	0.2	0.3	0.2	0.3	0.2
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		1.3		1.3		1.3	
Density(g/cm ³)		2.403		2.401		2.405	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		32		32		32	
Viscosity	Strain point (°C)	659		654		663	
	Annealing point (°C)	718		713		722	
	Softening point (°C)	977		974		986	
	10 ^{4.0} (°C)	1326		1320		1337	
	10 ^{3.0} (°C)	1512		1512		1514	
	10 ^{2.5} (°C)	1630		1602		1636	
Young's modulus		68		68		68	
Specific Young's modulus		28.3		28.3		28.3	
BHF resistance	Corrosion (μm)	0.4		0.4		0.4	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	4.5		4.6		2.6	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1150		1141		1128	
Liquidus viscosity		10 ^{5.5}		10 ^{5.5}		10 ^{5.8}	

[0068]

[Table 15]

		Sample No. 43		Sample No. 44		Sample No. 45	
		Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂		62.1	69.5	62.1	69.4	61.2	68.5
Al ₂ O ₃		15.3	10.1	15.3	10.1	15.8	10.4
B ₂ O ₃		11.4	11.0	11.4	11.0	11.8	11.4
MgO		-	-	-	-	0.5	0.8
CaO		5.9	7.1	5.9	7.1	5.4	6.5
SrO		1.0	0.7	1.5	1.0	1.0	0.7
BaO		3.0	1.3	2.5	1.1	3.0	1.3
ZnO		-	-	-	-	-	-
P ₂ O ₅		-	-	-	-	-	-
As ₂ O ₃		-	-	-	-	-	-
SnO ₂		-	-	-	-	-	-
Sb ₂ O ₃		1.0	0.2	1.0	0.2	1.0	0.2
ZrO ₂		0.3	0.2	0.3	0.2	0.3	0.2
Cl		-	-	-	-	-	-
(BaO + SrO)/BaO		1.3		1.6		1.3	
Density(g/cm ³)		2.401		2.402		2.404	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		32		33		32	
Viscosity	Strain point (°C)	660		661		659	
	Annealing point (°C)	721		721		718	
	Softening point (°C)	986		985		976	
	10 ^{4.0} (°C)	1331		1335		1319	
	10 ^{3.0} (°C)	1505		1517		1496	
	10 ^{2.5} (°C)	1610		1634		1600	
Young's modulus		68		68		69	
Specific Young's modulus		28.3		28.3		28.7	
BHF resistance	Corrosion (μm)	0.4		0.4		0.4	
	Visual appearance evaluation	○		○		○	
HC resistance	Corrosion (μm)	2.6		2.6		4.4	
	Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)		1112		1091		1150	
Liquidus viscosity		10 ^{6.0}		10 ^{6.2}		10 ^{6.4}	

[0069]

[Table 16]

		Sample No. 46	
		Mass %	mol%
SiO ₂		61.1	68.1
Al ₂ O ₃		16.5	10.8
B ₂ O ₃		10.3	9.9
MgO		-	-
CaO		7.8	9.3
SrO		1.5	1.0
BaO		0.6	0.3
ZnO		-	-
P ₂ O ₅		-	-
As ₂ O ₃		-	-
SnO ₂		-	-
Sb ₂ O ₃		2.0	0.5
ZrO ₂		0.2	0.1
Cl		-	-
(BaO + SrO)/BaO		3.5	
Density(g/cm ³)		2.395	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)		34	
Viscosity	Strain point (°C)	669	
	Annealing point (°C)	724	
	Softening point (°C)	975	
	10 ^{4.0} (°C)	1306	
	10 ^{3.0} (°C)	1472	
	10 ^{2.5} (°C)	1579	
Young's modulus		70	
Specific Young's modulus		29.0	
BHF resistance	Corrosion (μm)	0.6	
	Visual appearance evaluation	○	
HC resistance	Corrosion (μm)	4.5	
	Visual appearance evaluation	○	
Liquidus temperature (°C)		1050	
Liquidus viscosity		10 ^{6.5}	

[0070]

[Table 17]

	Sample No. 47		Sample No. 48		Sample No. 49	
	Mass %	mol%	Mass %	mol%	Mass %	mol%
SiO ₂	56.0	63.2	58.0	62.8	57.8	67.7
Al ₂ O ₃	11.0	7.3	20.0	12.8	16.4	11.3
B ₂ O ₃	15.0	14.6	13.0	12.2	8.5	8.6
MgO	-	-	4.0	6.5	0.7	1.2
CaO	8.0	9.7	5.0	5.8	4.1	5.1
SrO	4.0	2.6	-	-	1.9	1.3
BaO	6.0	2.7	-	-	9.4	4.3
ZnO	-	-	-	-	-	-
P ₂ O ₅	-	-	-	-	-	-
As ₂ O ₃	-	-	-	-	1.2	0.4
SnO ₂	-	-	-	-	-	-
Sb ₂ O ₃	-	-	-	-	-	-
ZrO ₂	-	-	-	-	-	-
Cl	-	-	-	-	-	-
(BaO + SrO)/BaO	1.6		0		2	
Density(g/cm ³)	2.529		2.351		2.554	
Thermal expansion coefficient [30-380°C] (x10 ⁻⁷ /°C)	45		30		38	
Viscosity	604		687		660	
Strain point (°C)	604		687		660	
Annealing point (°C)	649		732		716	
Softening point (°C)	840		972		968	
10 ^{4.0} (°C)	1119		1273		1310	
10 ^{3.0} (°C)	1313		1425		1480	
10 ^{2.5} (°C)	1405		1522		1588	
Young's modulus	66		75		71	
Specific Young's modulus	26.0		31.9		27.8	
BHF resistance	0.4		1.1		0.9	
Corrosion (μm)	0.4		1.1		0.9	
Visual appearance evaluation	○		○		○	
HC resistance	11.5		9.8		1.5	
Corrosion (μm)	11.5		9.8		1.5	
Visual appearance evaluation	○		○		○	
Liquidus temperature (°C)	1110		Above 1250		1090	
Liquidus viscosity	10 ^{4.0}		Below 10 ^{4.2}		10 ^{6.0}	

[0071] Each glass sample in the tables was prepared as follows. 40

[0072] First, a batch of glass raw materials was blended to achieve the compositions shown in the tables, placed in a platinum crucible, and melted at 1,600°C for 24 hours. The molten glass was then poured onto a carbon plate and formed into a sheet. The resulting glass samples were evaluated for various properties, including density, thermal expansion coefficient, viscosity, Young's modulus, specific Young's modulus, BHF resistance, HCl resistance, liquidus temperature, and liquidus viscosity, with the results shown in the tables.

[0073] As evident from the tables, the glass samples of the examples, No. 1-46, contain no alkali metal oxides, have 50

a density of 2.405 g/cm³ or less, a thermal expansion coefficient of 31-36×10⁻⁷/°C, and a strain point of 654°C or higher. Additionally, they exhibit a specific Young's modulus of 27.9 GPa/g·cm⁻³ or higher, excellent BHF resistance with an erosion of 0.8 μm or less, and HCl resistance with an erosion of 7.3 μm or less, with no changes observed in visual appearance evaluations. From this, it is understood that each sample of the examples is suitable for use as a glass substrate for TFT-LCDs.

[0074] Furthermore, these samples have a temperature corresponding to a high-temperature viscosity of 10^{2.5} dPa·s of 1,650°C or lower, making them easy to melt, and a liquidus temperature of 1,150°C or lower with a liquidus

viscosity of $10^{5.4}$ dPa·s or higher, indicating excellent devitrification resistance. This demonstrates that each sample of the examples also excels in productivity.

[0075] In contrast, the comparative example glass Sample No. 47 has a high density of 2.511 g/cm^3 , a high thermal expansion coefficient of $45 \times 10^{-7}/^\circ\text{C}$, and a low strain point of 604°C . Additionally, the erosion by HCl was large at $11.5 \text{ }\mu\text{m}$, and visual observation after HCl treatment revealed cloudiness and cracks. Similarly, the glass sample No. 48 exhibited significant erosion of $1.1 \text{ }\mu\text{m}$ by BHF and $9.8 \text{ }\mu\text{m}$ by HCl. Visual observation after BHF treatment showed surface roughness, and after HCl treatment, cloudiness was observed. Furthermore, its liquidus temperature was high at $1,250^\circ\text{C}$ or above, indicating poor devitrification resistance. Additionally, the glass Sample No. 49 (1737 glass) has a high density of 2.554 g/cm^3 , making it difficult to achieve large-sized and thin glass substrates. Its thermal expansion coefficient of $38 \times 10^{-7}/^\circ\text{C}$ is high, resulting in poor thermal shock resistance and a slight mismatch with the thermal expansion coefficient of TFT materials, which may cause warping.

[0076] Note that the density in the tables was measured using the well-known Archimedes method.

[0077] The thermal expansion coefficient was measured as the average thermal expansion coefficient in the temperature range of $30\text{--}380^\circ\text{C}$ using a dilatometer.

[0078] The strain point and annealing point were measured based on the method of ASTM C336-71. Higher values for these properties indicate greater heat resistance of the glass. The softening point was measured based on the method of ASTM C338-93. The temperatures corresponding to viscosities of $10^{4.0}$, $10^{3.0}$, and $10^{2.5}$ dPa·s were measured using the platinum sphere pull-up method. The temperature corresponding to the high-temperature viscosity of $10^{2.5}$ dPa·s indicates the melting temperature, with a lower temperature signifying better meltability.

[0079] The Young's modulus was measured using the resonance method, and the specific Young's modulus was calculated from the values of Young's modulus and density.

[0080] BHF resistance and HCl resistance were evaluated using the following method. First, both surfaces of each glass sample were optically polished, and a portion was masked. The samples were then immersed in a chemical solution prepared at a specified concentration, at a predetermined temperature, for a predetermined duration. After the chemical treatment, the mask was removed, and the step height between the masked and eroded portions was measured using a surface roughness tester, with this value taken as the degree of erosion. Additionally, after optically polishing both surfaces of each glass sample, the samples were immersed in a chemical solution prepared at a specified concentration, at a predetermined temperature, for a predetermined duration. The glass surface was then visually observed, and samples exhibiting cloudiness, roughness, or cracks were marked as $\times$, while those showing no changes were marked as $\circ$.

[0081] The chemical solutions and treatment conditions were as follows: For BHF resistance, the erosion was measured using a 130BHF solution (NH_4HF : 4.6 mass%, NH_4F : 36 mass%) at 20°C for 30 minutes. Visual appearance evaluation was conducted using a 63BHF solution (HF : 6 mass%, NH_4F : 30 mass%) at 20°C for 30 minutes. For HCl resistance, the erosion was measured using a 10 mass% hydrochloric acid aqueous solution at 80°C for 24 hours. Visual appearance evaluation was conducted using a 10 mass% hydrochloric acid aqueous solution at 80°C for 3 hours.

10 [0082] The liquidus temperature was determined by crushing each glass sample, sieving it to obtain glass powder that passes through a 30-mesh standard sieve ($500 \text{ }\mu\text{m}$) but is retained on a 50-mesh sieve ($300 \text{ }\mu\text{m}$), placing the powder in a platinum boat, and holding it in a temperature gradient furnace for 24 hours to measure the temperature at which crystals precipitate.

[0083] The liquidus viscosity indicates the viscosity of the glass at the liquidus temperature. A lower liquidus temperature and higher liquidus viscosity indicate superior devitrification resistance and better formability. To successfully form glass substrates for displays using the downdraw method, it is desirable for the liquidus temperature to be $1,150^\circ\text{C}$ or lower (preferably $1,100^\circ\text{C}$ or lower) and the liquidus viscosity to be $10^{5.4}$ dPa·s or higher (preferably 10^6 dPa·s or higher).

[0084] Additionally, the glass of Sample No. 36 from the examples was melted in a test melting furnace and formed using the overflow downdraw method to produce a display glass substrate with a thickness of 0.5 mm . This glass substrate exhibited a warp of 0.075% or less, a waviness (WCA) of $0.15 \text{ }\mu\text{m}$ or less (cutoff fh: 0.8 mm , fl: 8 mm), and a surface roughness (R_y) of $100 \text{ }\text{\AA}$ or less (cutoff λc : $9 \text{ }\mu\text{m}$), demonstrating excellent surface precision and suitability as a glass substrate for liquid crystal displays.

[0085]

[Effects of the Invention] As described above, the alkali-free glass of the present invention is substantially free of alkali metal oxides, has a density of 2.45 g/cm^3 or less, an average thermal expansion coefficient of $25\text{--}36 \times 10^{-7}/^\circ\text{C}$ in the temperature range of $30\text{--}380^\circ\text{C}$, and a strain point of 640°C or higher, resulting in low thermal contraction and deflection, excellent thermal shock resistance, and reduced likelihood of warping.

40 [0086] Furthermore, the alkali-free glass of the present invention has a low liquidus temperature and high liquidus viscosity, making it suitable for forming into sheets using the downdraw method. Additionally, it exhibits excellent chemical resistance, high specific Young's modulus, and superior meltability, making it suitable for glass substrates used in various electronic devices, particularly for flat display substrates, including glass substrates for a-Si TFT-LCDs and P-Si TFT-LCDs.

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F Term (Reference)

2H090	JB02	JC08	JC19	JD13	LA04	
4G062	AA01	BB01	DA01	DA02	DA03	
	DA06	DB01	DB02	DB03	DB04	
	DC03	DC04	DD01	DD02	DD03	
	DE01	DE02	DE03	DF01	EA01	
	EB01	EC01	ED01	ED02	ED03	
	EE03	EE04	EF01	EF02	EF03	10
	EG02	EG03	FA01	FA10	FB01	
	FB02	FB03	FC01	FC02	FC03	
	FD01	FE01	FE02	FE03	FF01	
	FG01	FG02	FG03	FH01	FJ01	
	FJ02	FJ03	FK01	FK02	FK03	
	FL01	FL02	FL03	GA01	GA10	
	GB01	GB02	GB03	GC01	GD01	
	GE01	GE02	GE03	HH01	HH03	
	HH05	HH07	HH09	HH11	HH12	
	HH13	HH15	HH17	HH20	JJ01	20
	JJ02	JJ03	JJ04	JJ05	JJ06	
	JJ07	JJ10	KK01	KK03	KK05	
	KK07	KK10	MM27	NN32	NN33	
	NN34	NN40				
5C094	AA36	BA03	BA43	EB02	FB02	
	FB03	HA08				