TRANSPERFECT

City of New York, State of New York, County of New York

I, Jacqueline Yorke, hereby certify that the document "**JP2004189535A**" is, to the best of my knowledge and belief, a true and accurate translation from Japanese into English.

Jacqueline Yorke

Sworn to before me this
December 24, 2024

Signature, Notary Public

WENDY POON
Notary Public - State of New York
No. 01PO0000184
Qualified in Queens County
My Commission Expires February 02, 2027

Stamp, Notary Public

(19) Japan Patent Office (JP)

(12) **Japanese Unexamined Patent Application Publication (A)**

(11) Japanese Unexamined Patent Application Publication Number

JP2004-189535 (P2004-189535A)

(43) Publication date: **July 8, 2004 (7/8/2004))**

(51) Int.Cl.7	FI	Theme Codes (Reference)
CO3C 3/091	CO3C 3/091	2H087
CO3C 3/093	CO3C 3/093	3K007
CO3C 3/11	CO3C 3 of 11	4G062
GO2F 1/1333	GO2F 1/1333 500	
HO5B 33/02	HO5B 33/02	
	Number of claims 3 OL Request for Examination: Not made	(13 pages in total) Continues on final page

(21) (21) Application number Japanese Patent Application No. 2005-50764 (P2005-50764)

(22) (22) Date of application: December 11, 2002 (12/11/2002)

(71) Applicant 000232243
Nippon Electric Glass Co., Ltd.
2-7-1 Haruhiki, Otsu-shi, Shiga Prefecture

(72) Inventor: Tomoyoshi Sanwa
2-7-1 Haruhiki, Otsu-shi, Shiga Prefecture
Inside Nippon Electric Glass Co., Ltd.

F term (reference) 2H090 JB02 JD01 JD09 JD18 LA04
3K007 AB03 AB17 AB18 CA01 DB03

Continued on the last page

(54)[Name of invention] Non-alkali glass substrate

(57) [Summary]

[Objective] The objective of the invention is to provide an alkaline-free glass substrate with high transmittance without increasing costs and which meets all required characteristics for liquid crystal displays.

[Constitution] The alkali-free glass substrate of this invention does not contain alkali metal oxides, and is characterized by the following: SnO_2 0.01-0.3%, As_2O_3 0-0.1%, Sb_2O3 0-1.0%, and the Fe content in the glass is 0.005-0.03% by mass, when converted to Fe_2O_3.

[Drawing selected] None

[Scope Patent Claims]

[Claim 1]

A non-alkali glass substrate that is virtually free of alkali metal oxides, and that contains 0.01 to 0.3% SnO_2, 0 to 0.1% As_2O_3, and 0 to 1.0% Sb_2O_3 by mass, and that contains 0.005 to 0.03% Fe_2O_3 by mass.

[Claim 2]

The non-alkali glass substrate according to Claim 1 is characterized in that the transmission rate of the glass substrate is 50% or more at a wavelength of 300 nm and 89% or more at a wavelength of 400 to 800 nm.

[Claim 3]

The characteristic feature of the invention is that it comprises SiO2 55-70%, Al2O3 12-20%, B2O3 5-15%, MgO 0-5%, CaO 0-12%, Sr O 0-10%, BaO 0-10%, ZnO 0-5%, ZrO2 0-5%, Cl 0-0.5% alkali-free glass substrate as described in either of the above Claims 1 or 2.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Use]

The present invention relates to substrates such as flat panel displays and sensors including liquid crystal displays, electroluminescent displays, field emission displays, etc., and non-alkali glass substrates used in cover glass of solid state imagers.

[0002]

[Prior Art]

Conventionally, rectangular glass substrates have been widely used as substrates such as flat panel displays and sensors, and as cover glass for solid-state image sensors.

[0003]

The surface of this type of glass substrate is coated with transparent conductive films, insulating films, semiconductor films, metal films, and the like, and various circuits and patterns are formed by photolithography etching (photoetching). In these deposition and photoetching steps, the glass substrate is subjected to hundreds of degrees of heat treatment and treated with various chemicals such as sulfuric acid, hydrochloric acid, alkaline solution, fustic acid, buffered fustic acid, and the like.

[0004]

The following properties are required of these glass substrates:

(1) When the glass contain alkali metal oxides, alkali ions diffuse into the deposited semiconductor material during heat treatment, leading to degradation of the film properties, to the extent that they substantially do not contain alkali metal oxides.

(2) The chemical resistance of the glass substrate is such that it does not degrade due to chemicals such as various acids and alkalis used in photo etching processes.

(3) In order to prevent pattern misalignment due to thermal shrinkage of the glass substrate in the TFT (thin film transistor) element manufacturing process, such as film deposition, the glass must have a high strain point, specifically a strain point of 640°C or higher. For example, in the case of a polycrystalline silicon TFT-LCD, the process temperature is 600°C or higher, so glass substrates for such applications are required to have a distortion point of 640°C or higher.

[0005]

In addition, the following characteristics are required.

(4) It must have excellent fusibility so that undesirable melting defects do not occur in the glass when it is used as a substrate.

(5) The coefficient of thermal expansion must be small in order to improve thermal shock resistance and reduce damage during the heat treatment process.

[0006]

Moreover, the transmittance of glass substrates is extremely important for these devices, and it is desirable that glass substrates have high transmittance in the ultraviolet to visible range.

[0007]
For example, in the case of liquid crystal displays, which are non-emissive displays, the efficiency of light utilization is poor, so it is better to have a the glass substrate be highly transmissive in the visible range. Also, TFT (thin film transistor) elements are formed by photolithography using a back exposure method that emits ultraviolet light at a wavelength of around 300 nm from the back surface of the glass substrate after deposition of transparent conductive films, insulating films, semiconductor films, metal films, etc. on the glass substrate. Therefore, it is better to have a higher transmission rate of the glass substrate in the ultraviolet region.
[0008]
In the case of organic electroluminescent displays, which have been attracting attention in recent years, the display is produced by emitting red, green and blue organic phosphors. However the luminous efficiency of the phosphor that emits blue light is lower than that of other phosphors. Thus, the transmission of glass in the wavelength range corresponding to blue light is higher.
[0009]
[Patent Citation 1]
JJP 7-202208 Publication
[Patent Citation 2]
Publication No. 2001-261366
[0010]
[Problems to be Solved by the Invention]
Fe_2O_3 is present in the state of Fe^{3+} or Fe^{2+} in glass, and in particular Fe^{3+} has an absorption peak near 380 nm, reducing the transmittance in the ultraviolet and short wavelength side visible regions. In general, inexpensive, mass-produced glass is entrained in glass with large amounts of Fe_2O_3 from glass raw materials and during the manufacturing process. Therefore, when this type of glass is used as a substrate for displays and sensors, the transmission rate in the ultraviolet and short wavelength visible regions is low, and there are concerns that the transmission rate will degrade the substrate's performance as a display and sensor.
[0011]
To completely eliminate Fe_2O_3 contamination in glass, it is necessary to use high-purity glass raw materials, and to use specially-designed manufacturing equipment that prevents Fe_2O_3 contamination in raw materials in the processing with raw material equipment, etc., which in turn results in higher manufacturing costs. Thus, this is not a realistic solution.
[0012]
The object of the present invention is to provide an alkaline-free glass substrate that satisfies all of the above requirements (1) to (5) and has a high transmittance without increasing costs.
[0013]
[Means of Solving the Problems]
In the course of repeated experimentation, the present inventor has found that the addition of SnO_2 to the glass yields the desired transmittance and those proposes this as the present invention.
[0014]
Thus, the alkali-free glass substrate of the present invention does not contain alkali metal oxides and is characterized by the fact that it contains 0.01 to 0.3% SnO2, 0 to 0.1% As2O3, and 0 to 1.0% Sb2O3 by mass%, and the content of Fe in the glass is 0.005 to 0.03% by mass%, when converted to Fe2O3.
[0015]
[Operation of the Invention]
Generally, when producing TFTs on a glass substrate, ultraviolet light with a wavelength centered on 300nm is used. Therefore, it is important that the transmittance of the glass substrate at a wavelength of 300 nm is as high as possible, at least 50% or more (preferably 60% or more). Transmittance levels of less than 50% may be time consuming and may interfere with productivity when back exposure is performed to form the TFT.
[0016]
Also, since liquid crystal displays are non-luminescent, it is better to have a lower loss of efficiency in using light. Therefore, it is important that the transmittance of the glass substrate for liquid crystal display in the visible range is as

high as possible, and that the transmittance at wavelengths of 400 to 800 nm be 89% or more (preferably 90% or more). Transmittance of less than 89% may reduce display performance.

[0017]

Thus, in the present invention, the alkali-free glass substrate has a limit of 0.1% or less for As2O3 in the glass, and 0.01% to 0.3% of SnO2 is added thereto. This changes the valence of Fe from +3 (Fe3+) to +2 (Fe2+) and maintains a transmittance of 50% or greater at a wavelength of 300 nm, while also maintaining a transmittance of 89% or more at a wavelength of 400 to 800 nm.

[0018]

When 0.01 to 0.3% SnO2 is added to glass, the reaction Sn2++2Fe3+→Sn4++2Fe2+ occurs, and it is believed that the valence of Fe changes, Fe2+ increases, and Fe3+ decreases, and the transmittance of the ultraviolet range and the short wavelength side of the visible range increases. If the SnO2 content is less than 0.01%, the amount of Fe that changes valence decreases, and the transmittance in the ultraviolet range and the short-wavelength side in the visible range decreases, which is not desirable. On the other hand, an SnO2 content greater than 0.3% is not desirable because SnO2 crystals tend to precipitate. The preferred range for SnO2 is 0.05 to 0.3%. In addition, there are other elements such as cerium and titanium that cause valence changes in iron in the same way as tin, but these are undesirable because they exhibit absorption in the ultraviolet range.

[0019]

In addition, As_2O_3, which is widely used as a clarifying agent, has an absorption peak in the ultraviolet region. As_3O_3 also inhibits SnO_2 from changing its valence to Fe^{2+}. Thus, the content of As_2O_3 is restricted to 0.1% or less. If the content of As_2O_3 is more than 0.1%, the transmittance in the ultraviolet range will decrease, which is undesirable. Preferably it is less than 0.05%. In alkaline-free glass, reducing the content of As_2O_3, which is used as a clarifying agent, makes it difficult to obtain a glass without bubbles, but because SnO_2, which is added to increase the transmittance, also acts as a clarifying agent, and glass without bubbles can be obtained by combining Sb_2O_3 and Cl as appropriate. However, as Sb_2O_3 also has an absorption peak in the ultraviolet region similar to As_2O_3, its content should be controlled to below 1.0%.

[0020]

Also, if Fe^{2+} is increased too much through the addition of SnO_2, since the absorption peak of 1080 nm of Fe^{2+} may reduce the visible transmission on the long wavelength side and prevent light transmission at wavelengths of 400 to 800 nm from being maintained at 89% or more. To prevent this, it is necessary to adjust the total Fe content, and it is important to keep it within the range of 0.005 to 0.03% when converted to Fe_2O_3. If the Fe_2O_3 content is greater than 0.03%, the visible transmittance on the long wavelength side decreases, which is not desirable. On the other hand, trying to reduce it to less than 0.005% is not desirable because the cost would be too high. The preferred range for Fe_2O_3 is 0.007 to 0.03%.

[0021]

The glass used in the present invention is non-alkali glass. The reason is that when alkali metal oxides (Na_2O, K_2O, Li_2O) are contained in glass, the alkali components in the glass not only degrade the properties of the various films and TFT elements formed on the glass substrate, but also the opacity of the alkali components and the various membranes react, which may decrease the transmittance of the substrate.

[0022]

The specific composition of the glass substrate of this invention can be determined as appropriate for each application, taking into account factors such as chemical resistance, thermal shrinkage, fusibility, moldability, and thermal expansion coefficient. As an example of suitable compositions, by mass percentage, are 55-70% SiO_2, 12-20% Al_2O_3, 5-15% B_2O_3, 0-5% MgO, 0-12% CaO 12%, SrO 0-10%, BaO 0-10%, ZnO 0-5%, ZrO 20-5%, and Cl 0-0.5% non-alkaline glass.

[0023]
The reasons for limiting the glass composition in this way are as follows:
[0024]
SiO_2 is a component that becomes a network former of glass, and has the effect of improving the acid resistance of glass and increasing the distortion point of glass to reduce heat shrinkage of glass substrates. If the content is between 55 and 70%, a glass substrate with high acid resistance and low heat shrinkage can be obtained. The preferred range is 57-67%. It should be noted that as the content of SiO_2 increases, the high temperature viscosity of the glass increases, and the meltability worsens, and cristobalites tend to precipitate more easily. Also, as SiO_2 content decreases, the acid resistance and distortion point of the glass tend to decrease.
[0025]
Al_2O_3 is a component that elevates the strain point of glass and suppresses the precipitation of devitrified inclusions in cristobalite. When its content is 12 to 20%, a glass substrate with a low liquid phase temperature can be obtained. The preferred range is 13-18%. As the content of Al_2O_3 increases, the buffered acid resistance of the glass tends to deteriorate, and the liquid phase temperature increases, making the glass difficult to mold. Also, as the content decreases, the distortion point of the glass tends to decrease.
[0026]
B_2O_3 is a component that acts as a melting agent, reducing the viscosity of the glass and improving meltability. The foregoing effects can be obtained when the content is between 5 and 15%. The preferred range is 7-14%. As the content of B_2O_3 increases, the distortion point of the glass tends to decrease and its acid resistance tends to worsen. In addition, when B_2O_3 content decreases, the melting properties tend to decrease without acting sufficiently as a melting agent.
[0027]
MgO is a component that improves the meltability of glass by reducing only high temperature viscosity without reducing the distortion point of the glass. The fusibility of glass can be improved when MgO content is 5% or less. The preferred range is 0-3%. Furthermore, as the MgO content increases, the loss of transparency in enstatite becomes more likely to occur. In addition, the resistance to buffered hydrofluoric acid is reduced and the glass substrate surface is eroded in the photo-etching process, and reactive organisms adhere to the glass substrate surface, making it easy for the glass substrate to become cloudy.
[0028]
CaO is a component that significantly improves the meltability of glass by reducing only high temperature viscosity without reducing the distortion point of the glass. The fusibility of glass can be improved when MgO content is 5% or less. The preferred range is 3-10%. As the CaO content increases, resistance to buffered acid tends to deteriorate.
[0029]
SrO is an ingredient that improves the chemical resistance and impermeability of glass. The foregoing effects can be obtained when the content is 10% or less. The preferred range is 0-7%. As the content of SrO increases, the density and coefficient of thermal expansion of the glass tend to increase and the fusibility tends to deteriorate.
[0030]
BaO, like SrO, is an ingredient that improves the chemical resistance and impermeability of glass. The foregoing effects can be obtained when the content is 10% or less. The preferred range is 0-5%. As the BaO content increases, the density of the glass and the coefficient of thermal expansion tend to increase, and its fusibility tends to deteriorate significantly.
[0031]
ZnO is a component that improves the buffered hydrofluoric acid resistance and fusibility of glass. The foregoing effects can be obtained when the content is 10% or less. The preferred range is 0-2.5%. Furthermore, as the ZnO content increases, the glass's resistance to loss of transparency and strain point tends to decrease.
[0032]
Furthermore, by mixing and including alkali earth metal oxides such as MgO, CaO, SrO, and BaO, it is possible to improve the fusibility and anti-leakage properties of glass, but if the total amount of these components increases, the density of the glass also tends to increase, making it difficult to reduce the weight of the glass substrate. It is therefore desirable to keep the total amount of additives to less than 11%.
[0033]

ZrO_2 is a component that improves the acid resistance of glass. When the content is 1% or less, the acid resistance of the glass can be improved. The preferred range is 0-0.7%. Furthermore, as the content of ZrO_2 increases, there is a tendency for of zircon devitrification to occur.

[0034]

Cl is a component that acts as a clarifying agent for glass. As Cl content increases, the amount of volatilization from the glass melt increases, and the occurrence of striae becomes more likely, but if the content is 0.5% or less, the above effects can be obtained without any problems. The preferred range is 0-0.4%.

[0035]

Next, methods of manufacturing the non-alkali glass substrates of the present invention will be described.

[0036]

First, the raw materials for the non-alkaline glass are selected while taking into consideration the amount of Fe contained as an impurity, and the raw materials are used to make a mixture that falls within the above-mentioned glass composition range. The raw materials thus prepared are then melted in a continuous melt furnace at a temperature of 1520 to 1680°C. After that, by forming molten glass into a sheet using methods such as the slot-die draw method, overflow-die draw method, float method, and roll-out method can be used and the glass is then slowly cooled to obtain an alkali-free glass substrate.

[0037]

[Embodiments]

The invention will be described in detail below based on embodiments thereof.

[0038]

Tables 1 to 4 show examples of the present invention (embodiments nos. 1 to 20), and Table 5 shows comparative examples (comparative examples nos. 21 and 22).

[0039]

[Table 1]

	Embodiment				
	1	2	3	4	5
Composition (mass percent)					
SiO_2	63.0	63.0	63.0	63.0	63.0
Al_2O_3	16.0	16.0	16.0	16.0	16.0
B_2O_3	11.0	11.0	11.0	11.0	10.0
MgO	–	–	–	–	–
CaO	7.0	7.0	7.0	7.0	8.0
SrO	1.5	1.5	1.5	1.5	1.0
BaO	0.5	0.5	0.5	0.5	1.0
ZnO	–	–	–	–	–
ZrO_2	–	–	–	–	–
SnO_2	0.1	0.1	0.1	0.1	0.1
AS_2O_3	–	–	–	–	–
Sb_2O_3	0.9	0.9	0.9	0.9	0.9
Cl	–	–	–	–	–
All Fe_2O_3	0.008	0.010	0.012	0.015	0.020
Transmittance (%) 300 nm	74	71	69	66	60
400 nm	92	91	91	91	90
600 nm	92	91	91	91	90
800 nm	92	92	92	92	91
Density (g/cm^3)	2.38	2.38	2.38	2.38	2.40
Coefficient of thermal expansion [30-380°C] ($\times 10^{-7}$/°C)	32	32	32	32	33
Strain point (°C)	675	675	675	675	676
Logn at $10^{2.5}$ (°C)	1610	1610	1610	1610	1595
Liquid phase temperature (°C)	1095	1095	1095	1095	1105
Acid resistance	○	○	○	○	○
Buffered hydrofluoric acid resistance	○	○	○	○	○

[0040]
[Table 2]

	Embodiment				
	6	7	8	9	10
Composition (mass percent)					
SiO_2	63.0	63.0	63.0	63.0	64.0
Al_2O_3	16.0	16.0	16.0	16.0	16.0
B_2O_3	10.0	12.0	12.0	12.0	11.0
MgO	–	–	–	–	–
Cao	8.0	8.0	8.0	8.0	8.0
SrO	1.0	–	–	–	0.5
BaO	1.0	–	–	–	0.1
ZnO	–	–	–	–	–
ZrO_2	–	–	–	–	–
SnO_2	0.1	0.2	0.05	0.15	0.2
AS_2O_3	–	–	–	–	–
Sb_2O_3	0.9	0.8	0.9	0.75	–
Cl	–	–	0.05	0.1	0.2
All Fe_2O_3	0.025	0.015	0.015	0.020	0.020
Transmittance (%) 300 nm	55	72	61	63	67
400 nm	90	91	91	91	91
600 nm	91	92	91	91	92
800 nm	91	92	92	92	92
Density (g/cm^3)	2.40	2.35	2.35	2.35	2.37
Coefficient of thermal expansion [30-380°C] ($\times 10^{-7}$/°C)	33	31	31	31	32
Strain point (°C)	676	670	668	671	670
Logn at $10^{2.5}$ (°C)	1595	1590	1590	1595	1600
Liquid phase temperature (°C)	1105	1080	1080	1080	1110
Acid resistance	○	○	○	○	○
Buffered hydrofluoric acid resistance	○	○	○	○	○

[0041]
[Table 3]

	Embodiment				
	11	12	13	14	15
Composition (mass percent)					
SiO_2	61.0	62.0	63.0	62.0	62.0
Al_2O_3	16.0	15.0	16.0	16.0	16.0
B_2O_3	12.0	9.4	12.0	11.0	11.0
MgO	−	0.5	−	−	1.3
Cao	7.0	7.0	7.0	8.0	8.0
SrO	1.9	4.0	1.0	0.5	1.0
BaO	1.0	0.05	0.3	1.5	0.5
ZnO	0.5	0.5	−	0.5	−
ZrO_2	−	0.4	−	0.15	−
SnO_2	0.1	0.25	0.15	0.15	0.1
AS_2O_3	−	0.1	−	−	−
Sb_2O_3	0.5	0.7	0.5	−	0.1
Cl	−	0.1	0.05	0.2	−
All Fe_2O_3	0.015	0.015	0.015	0.010	0.010
Transmittance (%) 300 nm	65	72	70	74	70
400 nm	91	91	91	92	91
600 nm	92	92	92	92	92
800 nm	92	92	92	92	92
Density (g/cm^3)	2.40	2.44	2.35	2.40	2.39
Coefficient of thermal expansion [30-380°C] ($\times 10^{-7}$/°C)	34	33	31	33	34
Strain point (°C)	665	671	668	669	673
Logn at $10^{2.5}$ (°C)	1555	1560	1605	1565	1560
Liquid phase temperature (°C)	1105	1055	1090	1085	1120
Acid resistance	○	○	○	○	○
Buffered hydrofluoric acid resistance	○	○	○	○	○

[0042]
[Table 4]

	Embodiment				
	16	17	18	19	2 0
Composition (mass percent)					
SiO_2	63.0	59.5	62.0	61.1	64.0
Al_2O_3	16.0	18.0	17.0	17.5	15.5
B_2O_3	9.5	10.5	10.0	9.5	9.0
MgO	−	−	0.3	−	0.7
Cao	9.0	8.0	8.5	5.5	6.5
SrO	1.0	−	0.5	3.5	2.0
BaO	0.5	3.0	1.5	0.5	−
ZnO	0.5	0.5	−	1.0	1.0
ZrO_2	−	0.2	−	0.3	0.5
SnO_2	0.15	0.15	0.15	0.1	0.1
AS_2O_3	−	−	−	−	−
Sb_2O_3	0.25	0.15	−	0.9	0.4
Cl	0.1	−	0.05	0.1	0.3
All Fe_2O_3	0.010	0.010	0.01	0.015	0.015
Transmittance (%) 300 nm	72	71	71	66	65
400 nm	91	91	91	91	91
600 nm	92	92	92	91	91
800 nm	92	92	92	92	92
Density (g/cm^3)	2.42	2.43	2.40	2.43	2.41
Coefficient of thermal expansion [30-380°C] ($\times 10^{-7}$/°C)	34	34	33	31	30
Strain point (°C)	677	680	682	686	685
Logn at $10^{2.5}$ (°C)	1585	1520	1585	1560	1605
Liquid phase temperature (°C)	1095	1115	1100	1115	1045
Acid resistance	○	○	○	○	○
Buffered hydrofluoric acid resistance	○	○	○	○	○

[0043]
[Table 5]

	Comparative Example	
	21	22
Composition (mass percent)		
SiO_2	62.0	58.5
Al_2O_3	16.0	15.0
B_2O_3	11.0	10.0
MgO	4.0	1.0
CaO	4.0	5.0
SrO	1.0	6.0
BaO	−	1.4
ZnO	−	−
ZrO_2	−	1.5
SnO_2	−	0.05
AS_2O_3	−	1.0
Sb_2O_3	2.0	0.5
Cl	−	0.05
All Fe_2O_3	0.020	0.030
Transmittance (%) 300 nm	40	39
400 nm	90	89
600 nm	90	89
800 nm	91	90
Density (g/cm^3)	2.38	2.49
Coefficient of thermal expansion [30-380°C] ($\times 10^{-7}$/°C)	30	37
Strain point (°C)	675	670
Logn at $10^{2.5}$ (°C)	1570	1460
Liquid phase temperature (°C)	1090	1230
Acid resistance	○	○
Buffered hydrofluoric acid resistance	x	○

[0044]

Each example in the tables was prepared as follows:

[0045]

First, the glass ingredients were mixed to form the compositions indicated in the table, and after melting at 1600℃ for 24 hours in a platinum pot, the mixtures were poured out onto a carbon plate and formed into plate shapes. Then, by optical polishing both sides of these plate-like glass, the vertical dimension is 300 mm, the horizontal dimension is 300 mm, and the thickness is 0. A 7 mm large, thin-walled glass substrate was made.

[0046]

The various characteristics of the plates were evaluated for each sample prepared in this manner. The results are shown in the table.

[0047]

As can be seen from the table, the transmittance of all of the test samples (No. 1 to 20) was high, at 55% or more at a wavelength of 300 nm, and 90% or more at wavelengths of 400 to 800 nm. The density was low at 2.43 g/cm3 or less,

making it possible to reduce the weight of the substrate. The coefficient of thermal expansion was 30-34×10^{-7}/°C. Because the strain point was high at 665°C or higher, a glass substrate with low heat shrinkage was obtained. In addition, the temperature corresponding to 102.5 poise is 1610°C or less, and the liquid phase temperature is 1120°C or less, so it also has excellent fusibility and formability. In addition, it showed excellent in acid resistance and BHF resistance.

[0048]

On the other hand, the comparative samples No. 21 and 22 had low transmittance of 40% or less at a wavelength of 300 nm.

[0049]

In terms of transmittance, the transmittance of the examples at wavelengths of 300 nm, 400 nm, 600 nm, and 800 nm was measured with a spectrophotometer.

[0050]

The density was measured using the well-known Archimedes' method.

[0051]

The coefficient of thermal expansion was measured using a dilatometer to determine the average coefficient of thermal expansion between 30 and 380°C.

[0052]

Strain point was measured according to the method of ASTM C336-71, and the higher the value, the smaller the heat shrinkage of the glass. The logη at $10^{2.5}$ indicates the temperature corresponding to a viscosity of $10^{2.5}$ poise, which is a high temperature viscosity. The lower this temperature, the better the meltability.

[0053]

Liquid phase temperature assessments were performed as follows. First, each sample was crushed to a size of 300-500μm, washed, and placed in a platinum boat, which was then transferred to a temperature gradient furnace at a temperature of 1000-1300°C and held for 24 hours. The platinum boat was then removed from the temperature gradient furnace. After that, the glass was removed from the platinum boat. The sample obtained in this way was observed under a polarizing microscope, and the point of crystallization was measured, which was taken as the liquid phase temperature.

[0054]

HCl resistance was assessed by immersing each sample in 10 wt% aqueous hydrochloric acid held at 80 °C for 3 hours and then visually observing surface condition. Resistance to buffered hydrofluoric acid was evaluated by immersing each sample in a buffered hydrofluoric acid solution (30% ammonium fluoride and 6% hydrofluoric acid) maintained at 20°C for 30 minutes, and then visually observing the surface condition of the sample. The surface of the glass substrate was marked with a circle with no change at all, and the color change was marked with a circle.

[0055]

[Advantageous Effects of the Invention]

As described above, the alkali-free glass substrate of this invention has a high transmittance across the entire visible spectrum, making it suitable for use as a glass substrate for flat panel displays, sensors, etc., and as a cover glass for solid-state image sensors. In addition, it has a high transmittance in the ultraviolet range, making it particularly suitable as an alkali-free glass substrate for use in TFT-type active matrix liquid crystal displays, which use backlight exposure to manufacture TFT elements.

Continued from front page

(51) Int.Cl.7		FI			Theme Codes (Reference)
H05B	33/14	H05B	33/14	A	

F term (reference) 4G062 AA01 BB05 BB06 DA06 DA07 DB04 DC03 DC04 DD01 DE01 DE02 DE03 DF01 EA01 EB01 EC01 ED01 ED02 ED03 EE01 EE02 EE03 EF01 EF02 EF03 EG01 EG02 EG03 FA01 FB01 FC01 FC02 FC03 FD01 FE01 FF01 FG01 FH01 FJ01 FK01 FL011 GA01 GA10 GB011 GD010GE01 HH03 HH01GC010 HH05 HH07 HH09 HH11 HH13 HH15 HH17 HH20 JJ01 JJ03 JJ05 JJ06 JJ07 JJ10 KK01 KK03 KK05 KK07 KK10 MM05 MM23 MM27 NN32 NN341