Alkali-free aluminoborosilicate glass, and uses thereof

The invention relates to an alkali-free aluminoborosilicate glass. The invention also relates to uses of this glass.

High requirements are placed on glasses for applications as substrates in flat-panel liquid-crystal display technology, for example in TN (twisted nematic)/STN (supertwisted nematic) displays, active matrix liquid-crystal displays (AMLCDs), thin-film transistors (TFTs) or plasma-addressed liquid crystals (PALCs). Besides high thermal shock resistance and good resistance to the aggressive chemicals employed in the process for the production of flat-panel screens, the glasses should have high transparency over a broad spectral range (VIS, UV) and, in order to save weight, a low density. Use as substrate material for integrated semiconductor circuits, for example in TFT displays ("chip on glass") in addition requires thermal matching to the thin-film material silicon which is usually deposited on the glass substrate in the form of amorphous silicon (a-Si) at low temperatures of up to 300°C. The amorphous silicon is partially recrystallized by subsequent heat treatment at temperatures of about 600°C. Owing to the a-Si fractions, the resulting, partially crystalline poly-Si layer is characterized by a thermal expansion coefficient of $\alpha_{20/300} \cong 3.7 \times 10^{-6}/K$. Depending on the a-Si/poly-Si ratio, the thermal expansion coefficient $\alpha_{20/300}$ may vary between $2.9 \cdot 10^{-6}/K$ and $4.2 \cdot 10^{-6}/K$. When substantially crystalline Si layers are generated by high temperature treatments above 700°C or direct deposition by CVD processes, which is likewise desired in thin-film photovoltaics, a substrate is required which has a significantly reduced thermal expansion of $3.2 \times 10^{-6}/K$ or less. In addition, applications in display and photovoltaics technology require the

absence of alkali metal ions. Sodium oxide levels of less than 1500 ppm as a result of production can be tolerated in view of the generally "poisoning" action due to diffusion of Na^+ into the semiconductor layer.

It should be possible to produce suitable glasses economically on a large industrial scale in adequate quality (no bubbles, knots, inclusions), for example in a float plant or by drawing methods. In particular, the production of thin (< 1 mm) streak-free substrates with low surface undulation by drawing methods requires high devitrification stability of the glasses. In order to counter compaction of the substrate during production, in particular in the case of TFT displays, which has a disadvantageous effect on the semiconductor microstructure, the glass needs to have a suitable temperature-dependent viscosity characteristic line: with respect to thermal process and shape stability, it should have a sufficiently high glass transition temperature, i.e. T_g > 700°C, while on the other hand not having excessively high melting and processing (V_A) temperatures, i.e. a V_A of ≤ 1350°C.

The requirements placed on glass substrates for LCD display technology or thin-film photovoltaics technology are also described in "Glass substrates for AMLCD applications: properties and implications" by J. C. Lapp, SPIE Proceedings, Vol. 3014, invited paper (1997), and in "Photovoltaik - Strom aus der Sonne" by J. Schmid, Verlag C. F. Müller, Heidelberg 1994, respectively.

From the production point of view, the transition to larger display formats places new requirements on the mechanical stability and the specific gravity of the glass substrates. The transition from present-day 600 mm x 720 mm sheets to sheets having dimensions of e.g. 1 m x 1 m and more would lead to a corresponding

increase in weight which would have an effect on, inter alia, the robot handling for transporting the glass sheet from one production process step to another. To minimize "elastic sagging", i.e. sagging of the sheets under their own weight, a glass is desirable which has a high modulus of elasticity of > 80 GPa, preferably ≥ 85 GPa, combined with a low density of < 2.55 g/cm^3. This also minimizes the risk of sagging of the sheet during coating of the glass substrate with an active silicon layer.

The glasses described in "Mechanical Properties of AMLCD Glass Substrates", Proceedings of the XVIII International Congress on Glass, San Francisco, CA, USA, July 5-10, 1998, have distinct disadvantages in this respect.

The same applies to the display or solar cell substrate glasses described in the following documents.

They do not meet the full list of requirements for the abovementioned applications.

Numerous documents describe glasses which are free of MgO or low in MgO and therefore do not have the required high mechanical stability, for example WO 97/11919, WO 97/11920, US 5,374,595, WO 00/32528, JP 9-156953A, JP 10-72237 A, EP 714 862 B, EP 341 313 B, DE 196 03 698 C1, DE 196 17 344 C1, DE 42 13 579 A and WO 98/27019.

Some of these glasses and also the glasses of DE 197 36 912 C1 and, according to the examples, the glasses of JP 9-48 632 A contain relatively high amounts of the heavy alkaline earth metal oxides BaO and/or SrO which leads to poor meltability. Moreover, such glasses have an undesirably high density, which is disadvantageous in particular for large-format

displays.

Glasses having high boric acid contents, as described in JP 8-295530 A, are easy to melt owing to their low melting temperatures, but have insufficient heat resistance and chemical resistance, in particular to hydrochloric acid solutions. Moreover, they have rather low moduli of elasticity.

DE 196 01 022 A1 describes SnO-containing glasses which are selected from a very wide composition range. The glasses, which, according to the examples, are low in MgO, rich in B_2O_3 and rich in BaO, tend to exhibit glass defects because of the ZrO_2 level which has to be present.

In the unexamined Japanese publications JP 10-25132 A, JP 10-114538 A, JP 10-130034 A, JP 10-59741 A, JP 10-324526 A, JP 11-43350 A, JP 11-49520 A, JP 10-231139 A, JP 10-139467 A, JP 11-292563 A and JP 2000-159541 A, mention is made of very wide composition ranges for display glasses, which can be varied by means of many optional components and which are admixed with one or more specific refining agents in each case. However, these documents do not indicate how glasses having the complete requirement profile described above can be obtained in a specific manner.

It is an object of the present invention to provide glasses which meet said complex requirement profile, with respect to physical and chemical properties, which is imposed on glass substrates for liquid-crystal displays, in particular for TFT displays, and for thin-film solar cells, in particular on the basis of polycrystalline Si, glasses which have high heat resistance, a favourable processing range, high chemical resistance and in particular sufficient mechanical stability.

The object is achieved by an aluminoborosilicate glass from the composition range as defined in the independent claim.

A first aspect of the invention provides an alkali-free aluminoborosilicate glass which has the following composition (in % by weight, based on oxide):

SiO_2	> 58 - 70
B_2O_3	0.5 - < 9
Al_2O_3	10 - 25
MgO	> 8 - 15
CaO	0 - < 10
SrO	0 - < 3
BaO	0 - < 2
with MgO + CaO + SrO + BaO	> 8 - 18
ZnO	0 - < 2

A second aspect of the invention provides use of the aluminoborosilicate glass according to the first aspect as substrate glass in display technology, in thin-film photovoltaics and for the preparation of a substrate glass for hard disks.

The glass contains > 58 - 70% by weight of SiO_2. At lower contents, the chemical resistance is impaired, while at higher levels, the thermal expansion becomes too low and the crystallization tendency of the glass 10 increases. Preference is given to a maximum content of 68% by weight.

The glass contains 10 - 25% by weight of Al_2O_3. This has a positive effect on the devitrification stability of the glass and the heat resistance increases without excessively increasing the processing temperature. Preference is given to a content of 14 - 24% by weight

of Al_2O_3.

The B_2O_3 content is 0.5 - < 9% by weight. The B_2O_3 content is restricted to the maximum content specified in order to achieve a high mechanical stability. Higher contents would also impair the chemical resistance to hydrochloric acid solutions. The minimum B_2O_3 content specified serves to ensure that the glass has good meltability and good devitrification stability. Preference is given to a content of 1 - 8.5% by weight. Particular preference is given to a maximum content of 5% by weight.

An essential glass component are the network-modifying alkaline earth metal oxides. With a sum of alkaline earth metal oxides of between > 8 and 18% by weight, a coefficient of thermal expansion $a_{20/300}$ of between 2.8 x 10^{-6}/K and 3.9 x 10^{-6}/K is achieved. MgO is always present, while CaO, SrO and BaO are optional components. Preferably at least two alkaline earth metal metal oxides are present. This second alkaline

earth oxide is particularly preferably CaO. Particularly preferably at least three alkaline earth metal oxides are present.

The glass contains > 8 - 15% by weight of MgO. These relatively high levels make it possible to obtain a glass having a modulus of elasticity which is sufficient for the increased requirements, and a low density.

The B_2O_3 content preferably depends on the MgO content because B_2O_3 and MgO have opposite effects on the modulus of elasticity. The MgO/B_2O_3 ratio by weight is thus preferably > 1, particularly preferably > 1.35.

Still higher MgO contents lead to a deterioration of the good crystallization stability and the high chemical HCl resistance of the glass.

The glass may furthermore contain up to < 10%, preferably < 9%, by weight of CaO. Higher levels would lead to an excessive increase in density and to an increase in crystallization tendency. It is preferred that the glass contains CaO, specifically preferably in an amount of at least 0.5% by weight, particularly preferably at least 1% by weight.

The glass may furthermore contain BaO, which has a positive effect on its devitrification stability. The maximum content is restricted to < 2% by weight to keep the density of the glass low. The BaO content of the glass is particularly preferably between 0 and 0.5% by weight. When a very lightweight glass is required, the glass is most preferably free of BaO.

The glass may furthermore contain SrO. Its presence likewise has a positive effect on the devitrification stability. The maximum SrO content is restricted to

< 3% by weight to keep the density of the glass low. The glass contains particularly preferably between 0 and 1% by weight and most preferably between 0 and 0.5% by weight.

The sum of the two heavy alkaline earth metal oxides SrO and BaO is preferably limited to a maximum of 4% by weight.

The glass may furthermore contain up to < 2% by weight of ZnO. ZnO has an effect on the viscosity characteristic line which is similar to that of boric acid, has a network-loosening function and has less effect on the thermal expansion than the alkaline earth metal oxides. The maximum ZnO level is preferably limited to 1.5% by weight, in particular when the glass is processed by the float method. Higher levels would increase the risk of unwanted ZnO coatings on the glass surface which may form by evaporation and subsequent condensation in the hot-shaping range.

The glass is alkali-free. The term "alkali-free" as used herein means that it is essentially free from alkali metal oxides, although it can contain impurities of less than 1500 ppm.

The glass may contain up to 2% by weight of ZrO_2 + TiO_2, where both the TiO_2 content and the ZrO_2 content can each be up to 2% by weight. ZrO_2 advantageously increases the heat resistance of the glass. Owing to its low solubility, ZrO_2 does, however, increase the risk of ZrO_2-containing melt relicts, so-called zirconium nests, in the glass. ZrO_2 is therefore preferably omitted. Low ZrO_2 contents originating from the corrosion of zirconium-containing trough material are unproblematic. TiO_2 advantageously reduces the solarization tendency, i.e. the reduction in transmission in the visible wavelength region because

of UV-VIS radiation. At contents of greater than 2% by weight, colour casts can occur due to complex formation with Fe^{3+} ions which are present in the glass at low levels as a result of impurities of the raw materials employed.

The glass may contain conventional refining agents in the usual amounts: it may thus contain up to 1.5% by weight of As_2O_3, Sb_2O_3, SnO_2, CeO_2, Cl^-, F^- and/or SO_4^{2-}. The sum of the refining agents should, however, not exceed 1.5% by weight. If the refining agents As_2O_3 and Sb_2O_3 are omitted, the glass can be processed not only using a variety of drawing methods, but also by the float method.

For example with regard to easy batch preparation, it is advantageous to be able to omit both ZrO_2 and SnO_2 and still obtain glasses having the property profile mentioned above, in particular having high heat and chemical resistance and low crystallization tendency.

Working examples:

Glasses were produced in Pt/Ir crucibles at 1620°C from conventional raw materials which were essentially alkali-free apart from unavoidable impurities. The melt was refined at this temperature for one and a half hours, then transferred into inductively heated platinum crucibles and stirred at 1550°C for 30 minutes for homogenization. The melts were poured into preheated graphite moulds and cooled down to room temperature.

The table shows eight examples of glasses according to the invention (A1 - A8) and an example of a comparative glass (C) with their compositions (in % by weight, based on oxide) and their most important properties. The following properties are given:

- the coefficient of thermal expansion $\alpha_{20/300}$ [10^{-6}/K]
- the density ρ [g/cm^3]
- the dilatometric glass transition temperature T_g [°C] in accordance with DIN 52324
- the temperature at a viscosity of 10^4 dPas (referred to as T 4 [°C])
- the modulus of elasticity E [GPa]
- an acid resistance "HCl" as weight loss (material removal value) from glass plates measuring 50 mm × 50 mm × 2 mm polished on all sides after treatment with 5% strength hydrochloric acid for 24 hours at 95°C [mg/cm^2]
- an alkali resistance "NaOH" as weight loss (material removal value) from glass plates measuring 50 mm × 50 mm × 2 mm polished on all sides after treatment with 5% strength aqueous sodium hydroxide solution for 6 hours at 95°C [mg/cm^2]
- a resistance "BHF" to buffered hydrofluoric acid as weight loss (material removal value) from glass plates measuring 50 mm × 50 mm × 2 mm polished on all sides after treatment with 10% strength $NH_4F \cdot HF$ solution for 20 minutes at 23°C [mg/cm^2].

Table

Examples: Compositions (in % by weight, based on oxide) and essential properties of glasses according to the invention (A1 - A8) and a comparative glass (C).

	A1	A2	A3	A4	A5
SiO_2	62.1	61.1	62.1	61.1	63.0
B_2O_3	4.0	5.0	3.0	5.0	6.0
Al_2O_3	17.4	17.9	18.4	17.9	15.9
MgO	10.0	9.0	11.0	9.0	8.1
CaO	5.1	5.6	5.1	5.6	5.6
SrO	1.0	-	-	0.8	0.8
BaO	-	1.0	-	0.2	0.2
ZnO	-	-	-	-	-
As_2O_3	-	-	-	-	-
SnO_2	0.4	0.4	0.4	0.4	0.4
$\alpha_{20/300}$ [10^{-6}/K]	3.76	3.72	3.78	3.75	3.67
T_g [°C]	745	739	749	739	725
ρ [g/cm^3]	2.52	2.513	2.53	2.510	2.486
T 4 [°C]	1227	1225	1225	1222	1228
E [GPa]	88	87	91	87	85
HCl [mg/cm^2]	0.09	0.19	0.07	0.20	0.21
NaOH [mg/cm^2]	1.0	1.1	1.0	n.m.	n.m.
BHF [mg/cm^2]	0.93	n.m.	0.92	n.m.	n.m.

n.m. = not measured

Continuation of table:

	A6	A7	A8	C
SiO_2	65.5	62.0	65.4	62.2
B_2O_3	5.0	6.5	2.5	6.3
Al_2O_3	16.4	16.4	16.4	15.0
MgO	8.5	9.0	8.5	6.4
CaO	2.0	4.5	7.0	4.5
SrO	2.0	-	-	5.2
BaO	0.2	-	-	-
ZnO	-	0.9	-	-
As_2O_3	-	-	0.2	-
SnO_2	0.4	0.7	-	0.4
$\alpha_{20/300}$ [10^{-6}/K]	3.28	3.48	3.75	3.84
T_g [°C]	738	721	748	714
ρ [g/cm^3]	2.468	2.447	2.502	2.521
T4 [°C]	1266	1217	1253	1238
E [GPa]	85	85	88	80
HCl [mg/cm^2]	0.18	0.35	0.04	n.m.
NaOH [mg/cm^2]	n.m.	n.m.	n.m.	n.m.
BHF [mg/cm^2]	n.m.	n.m.	n.m.	n.m.

n.m. = not measured

As the working examples illustrate, the glasses according to the invention have the following advantageous properties:

- a thermal expansion $\alpha_{20/300}$ of between 2.8 x 10^{-6}/K and 3.9 x 10^{-6}/K, thus matched to the expansion behaviour of polycrystalline silicon.

- with T_g > 710°C, a high glass transition temperature, i.e. a high heat resistance. This is essential for the lowest possible compaction as a result of production and for use of the glasses as substrates for coatings with amorphous Si layers and their subsequent annealing.

- with ρ < 2.55 g/cm^3, a low density.

- with E > 80 GPa, a high modulus of elasticity. This modulus or the high specific modulus of elasticity, E/ρ, ensures sufficient mechanical stability, in particular with regard to the sagging problem.

- a temperature at a viscosity of 10^4 dPas (processing temperature V_A) of at most 1300°C, and a temperature at a viscosity of 10^2 dPas of at most 1700°C, which means that the glasses have a suitable viscosity characteristic line with regard to hot-shaping and meltability, using conventional methods.

- a high chemical resistance, as is evident inter alia from excellent resistance to hydrochloric acid solutions, which makes them sufficiently inert to the chemicals used in the production of flat-panel screens.

With these properties, the glasses are thus highly suitable for use as substrate glass in display technology, in particular for TFT displays, and in

thin-film photovoltaics, in particular on the basis of polycrystalline Si, and as substrate glass for hard disks.

PATENT CLAIMS

1. Alkali-free aluminoborosilicate glass which has the following composition (in % by weight, based on oxide):

SiO_2	> 58 - 70
B_2O_3	0.5 - < 9
Al_2O_3	10 - 25
MgO	> 8 - 15
CaO	0 - < 10
SrO	0 - < 3
BaO	0 - < 2
with MgO + CaO + SrO + BaO	> 8 - 18
ZnO	0 - < 2

2. Aluminoborosilicate glass according to Claim 1, characterized by the following composition (in % by weight, based on oxide):

SiO_2	> 58 - 68
B_2O_3	1 - 8.5
Al_2O_3	14 - 24
MgO	> 8 - 15
CaO	0 - 9
SrO	0 - < 3
BaO	0 - < 2
with MgO + CaO + SrO + BaO	> 8 - 18
ZnO	0 - < 2

3. Aluminoborosilicate glass according to Claim 1 or 2, characterized in that it comprises between 0 and 0.5% by weight of BaO.

4. Aluminoborosilicate glass according to at least one of Claims 1 to 3, characterized in that it comprises between 0 and 1% by weight of SrO, preferably between 0 and 0.5% by weight of SrO.

5. Aluminoborosilicate glass according to at least one of Claims 1 to 4, characterized in that it comprises at most 5% by weight of B_2O_3.

6. Aluminoborosilicate glass according to at least one of Claims 1 to 5, characterized in that it additionally comprises:

ZrO_2	0 - 2
TiO_2	0 - 2
with $ZrO_2 + TiO_2$	0 - 2
As_2O_3	0 - 1.5
Sb_2O_3	0 - 1.5
SnO_2	0 - 1.5
CeO_2	0 - 1.5
Cl^-	0 - 1.5
F^-	0 - 1.5
SO_4^{2-}	0 - 1.5
with $As_2O_3 + Sb_2O_3 + SnO_2 + CeO_2 + Cl^- + F^- + SO_4^{2-}$	≤ 1.5

7. Aluminoborosilicate glass according to at least one of Claims 1 to 6, which has a coefficient of thermal expansion $\alpha_{20/300}$ of between $2.8 \cdot 10^{-6}/K$ and $3.9 \cdot 10^{-6}/K$, a glass transition temperature Tg of > 710°C, a density ρ of < 2.55 g/cm^3 and an "acid resistance HCl" of < 0.5 mg/cm^2.

8. Aluminoborosilicate glass according to at least one of Claims 1 to 7, has a modulus of elasticity of more than 80 GPa.

9. Use of the aluminoborosilicate glass according to at least one of Claims 1 to 8 as substrate glass in display technology.

10. Use of the aluminoborosilicate glass according to

at least one of Claims 1 to 8 as substrate glass in thin-film photovoltaics.

11. Use of the aluminoborosilicate glass according to at least one of Claims 1 to 8 for the preparation of a substrate glass for hard disks.