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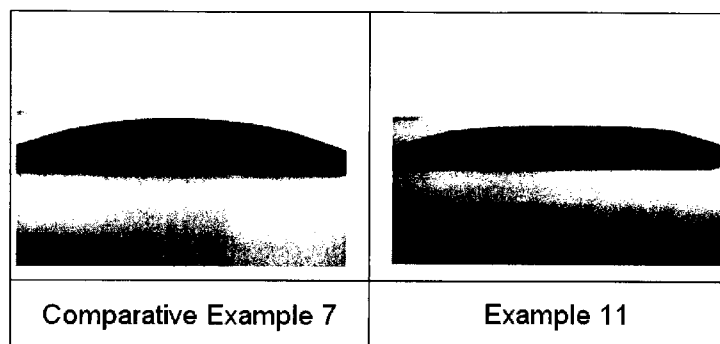
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(54) Title: ZNO-BASED GLASS FRIT COMPOSITION AND ALUMINUM PASTE COMPOSITION FOR BACK CONTACTS
OF SOLAR CELL USING THE SAME

FIG. 1



(57) Abstract: This disclosure relates to a ZnO-based glass frit composition and an aluminum paste composition for back contact of a solar cell using the same, more particularly, to a glass frit composition for forming an aluminum paste for back contact of a solar cell that essentially comprises P205 and BaO in specific content ranges, is used as an inorganic binder in the aluminum paste composition during manufacture of back contact of a solar cell to minimize bowing of a substrate due to shrinkage difference at cooling after firing of the substrate, thereby preventing break of the substrate, exhibits moisture stability of the aluminum fired film, and may improve open circuit voltage and photoconversion efficiency of a battery, and an aluminum paste composition using the same.



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TITLE OF THE INVENTION

ZNO-BASED GLASS FRIT COMPOSITION AND ALUMINUM PASTE
COMPOSITION FOR BACK CONTACTS OF SOLAR CELL USING THE SAME

BACKGROUND OF THE INVENTION**(a) Field of the Invention**

This disclosure relates to a ZnO-based glass frit composition that may minimize bowing of a substrate after firing and exhibits moisture stability in the manufacture of back contact of a solar cell, and improve open circuit voltage and photoconversion efficiency, and an aluminum paste composition for back contact of a solar cell using the same.

(b) Description of the Related Art

A solar cell recently attracts attention because energy resources are abundant and there is no problem of environmental pollution. A solar cell has a junction structure of p-type semiconductor and n-type semiconductor. If light enters into a solar cell, by the interaction of light and material constituting the semiconductor of the solar cell, negatively charged electrons get out and positively charged holes are generated, and while they move, current flows. Specifically, electrons are attracted to n-type semiconductor, and holes are attracted to p-type semiconductor, and thus, respectively move to an n-type electrode bonded with n-type semiconductor and a p-type electrode bonded with p-type semiconductor. If the electrodes are connected by wires, electricity flows to obtain electric power.

And, the solar cell is divided into a silicon solar cell and a compound semiconductor solar cell according to material and manufacturing technology, and into a substrate-type and a thin film-type according to material.

Meanwhile, the silicon solar cell is formed by printing a paste including conductive metal on a substrate, drying and firing, and to form back contact, aluminum powder is mostly used.

The aluminum paste including the aluminum powder may be used for manufacturing a solar cell with high conversion efficiency. And, the aluminum paste is divided into lead-containing and lead-free. The lead-containing aluminum paste includes lead-containing glass frit, and it may realize high conversion efficiency. However, since the lead-containing glass frit raises an environmental problem, it is a recent trend to convert to a method of using lead-free glass frit in the aluminum paste.

The lead-free glass composition commonly uses bismuth-based (Bi_2O_3) glass. The basic ingredient is Bi_2O_3 , and Al_2O_3 , B_2O_3 , SiO_2 are included during cast molding of glass. And, as additional ingredients, at least one selected from Fe_2O_3 , P_2O_5 , MgO , Ga_2O_3 , Li_2O , Na_2O , ZrO_2 , AgO , Sc_2O_3 , SrO , BaO , CaO , Pd , Pt and Rh are used in the composition.

However, the bismuth-based glass composition uses expensive Bi_2O_3 , generates substrate bowing due to high coefficient of thermal expansion to increase break rate of the wafer, and has low moisture stability or exhibit comparatively low battery efficiency.

SUMMARY OF THE INVENTION

The present invention provides a ZnO-based glass frit composition that is used as an inorganic binder in an aluminum paste composition to minimize bowing of a substrate due to shrinkage difference at cooling after firing of the substrate, thereby preventing break of the substrate in the manufacture of back contact of a solar cell, exhibits moisture stability to prevent

discoloration of the aluminum fired film due to moisture, and increase open circuit voltage and improve photoconversion efficiency of a battery.

The present invention also provides a lead-free aluminum paste composition for forming back contact of a solar cell that uses the glass frit composition as an inorganic binder to improve battery characteristics.

The present invention provides a glass frit composition for forming an aluminum paste for back contact of a solar cell comprising:

- (a) 45 to 60 wt% of ZnO,
- (b) at least one metal oxide selected from the group consisting of 0.1 to 45 wt% of SiO₂, 0.1 to 40 wt% of B₂O₃, and 1 to 10 wt% of Al₂O₃,
- (c) 0.1 to 20 wt% of transition metal oxide, lanthanide oxide, or a mixture thereof,
- (d) 3 to 5 wt% of P₂O₅, and
- (e) 3 to 5 wt% of BaO.

The glass frit composition may have an average particle size of 0.5 to 20 μm , moisture content of 5% or less, and coefficient of thermal expansion of $50 \times 10^{-7}/^{\circ}\text{C}$ to $150 \times 10^{-7}/^{\circ}\text{C}$.

The transition metal oxide is at least one selected from the group consisting of MnO, MnO₂, Co₃O₄, Co₂O₃, CoO, TiO₂, V₂O₅ and CuO. And, the lanthanide oxide is at least one selected from the group consisting of CeO₂, Pr₂O₃, Eu₂O₃, Tb₂O₃, Nd₂O₃ and Sm₂O₃.

The present invention also provides a lead-free aluminum paste composition for forming back contact of a solar cell comprising aluminum powder, an inorganic binder and an organic vehicle,

wherein the aluminum paste composition includes the above ZnO-based glass frit composition as the inorganic binder.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photograph showing the results of bowing evaluation of Comparative Example 7 and Example 11.

Fig. 2 is a photograph showing the results of moisture reaction stability of Comparative Example 8 and Example 11.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Hereinafter, the present invention will be explained in detail

The present invention relates to a ZnO-based glass frit composition that may be used as an inorganic binder in a composition for forming back contact of a solar cell. The present invention also provides a lead-free aluminum paste composition using the glass frit composition, which is suitable for use in the formation of back contact of a solar cell.

Unlike the existing glass frit composition including PbO or bismuth as a main ingredient, the present invention provides a lead-free glass frit composition that does not include bismuth.

Thus, the glass frit composition of the present invention includes ZnO as a main ingredient, and includes at least one of SiO₂, B₂O₃ and Al₂O₃ for the formation of glass. And, the glass frit composition of the present invention includes a compound including at least one transition metal element of Mn, Co, Cu, Ti, and V, and/or a compound including at least one lanthanide element of Ce, Pr, Eu, Tb, Nd, and Sm, and P₂O₅ and BaO in specific content ranges,

for controlling of electrical property (conversion efficiency) and moisture reactivity of a substrate.

As such, since the present invention uses a glass frit composition with a specific composition, a composition having lower coefficient of thermal expansion than the existing bismuth-based composition may be formed to largely reduce the substrate bowing and break due to shrinkage difference at firing and cooling of the substrate. Moreover, the present invention is eco-friendly because it does not include a lead ingredient, and it may largely reduce cost because it does not use an expensive bismuth compound and uses ZnO-based glass frit using easily available metal oxide. Further, the present invention may be effective for forming a back P++layer on a p-type substrate to increase open circuit voltage, by including at least one oxide of transition metal selected from the group consisting of Mn, Co, Cu, Ti and V and/or at least one oxide of lanthanide selected from the group consisting of Ce, Pr, Eu, Tb, Nd and Sm. This is connected with voltage (Voc) increase between upper and lower ends of the substrate to increase conversion efficiency. In addition, since the present invention includes P₂O₅ and BaO in specific content ranges, moisture stability and bowing of a substrate may be further improved.

According to a preferred embodiment of the present invention, provided is a glass frit composition for forming an aluminum paste of back contact of a solar cell comprising (a) 45 to 60 wt% of ZnO, (b) at least one metal oxide selected from the group consisting of 0.1 to 45 wt% of SiO₂, 0.1 to 40 wt% of B₂O₃ and 1 to 10 wt% of Al₂O₃, (c) 0.1 to 20 wt% of transition metal oxide, lanthanide oxide or a mixture thereof, (d) 3 to 5 wt% of P₂O₅, and (e) 3 to 5 wt% of BaO.

And, according to a most preferred embodiment of the present invention, provided is a glass frit composition for forming an aluminum paste of back contact of a solar cell comprising

(a) 45 to 60 wt% of ZnO, (b) at least one metal oxide selected from the group consisting of 6 to 18 wt% of SiO₂, 4 to 17wt% of B₂O₃, and 5 to 10 wt% of Al₂O₃, (c) 0.1 to 20 wt% of transition metal oxide, lanthanide oxide or a mixture thereof, (d) 3 to 5 wt% of P₂O₅, and (e) 3 to 5 wt% of BaO.

The glass frit composition having the specific composition is used for preparing an aluminum paste composition for forming back contact of a solar cell, instead of being used for PDP as previously known. Thus, the present invention may prevent discoloration of an aluminum fired film by moisture due to excellent moisture stability, as well as bowing of a substrate, thus largely increasing open circuit voltage and photoconversion efficiency of a solar cell.

Meanwhile, in the glass frit composition of the present invention, (a) ZnO is used as a main ingredient, forms a backbone structure with other constitutional ingredients to increase stability, thus increasing thermal stability, water-proofing and moisture resistance. The ZnO content may be preferably 45 to 60 wt% based on the total glass frit composition, more preferably 45 to 55 wt%. If the ZnO content is less than 45 wt%, relative ratios of other ingredients may be increased and thus viscosity required for glass flow may not be obtained, and if it exceeds 60 wt%, glass formation may be difficult or glass may be excessively cured to increase glass transition temperature. Thus, the ZnO should be included in the glass frit composition in the above content so as to contribute to physical properties improvement.

And, in the glass frit composition of the present invention, the ingredient (b) plays a basic function for stably forming the glass frit. And, the at least one metal oxide selected from the group consisting of SiO₂, B₂O₃ and Al₂O₃ may be preferably used in a combination, and for

example, a mixture of 2 or 3 kinds selected from SiO_2 , B_2O_3 and Al_2O_3 may be included. The SiO_2 is used to lower coefficient of thermal expansion and gellation frequency of the glass, the Al_2O_3 is used to decrease crystallization of glass and coefficient of thermal expansion and increase chemical durability of the glass, and the B_2O_3 is used to lower coefficient of thermal expansion and increase stability of the glass. The (b) metal oxide may respectively include 0.1 to 45 wt% of SiO_2 , 0.1 to 40 wt% of B_2O_3 , and 1 to 10 wt% of Al_2O_3 , more preferably 6 to 18 wt% of SiO_2 , 4 to 17 wt% of B_2O_3 , and 5 to 10 wt% of Al_2O_3 , based on total glass frit composition. And, at least one kind may be selected and used, and a mixture of 2 or 3 kinds selected from SiO_2 , B_2O_3 and Al_2O_3 may be used, as explained above. These are basic ingredients for forming glass, and if the contents are less than or exceed the above ranges, glass formation may be difficult.

And, in the glass frit composition of the present invention, the ingredient (c) is effective for formation of p^{++} layer of back contact on a p-type substrate and thus may improve photoconversion efficiency and open circuit voltage of a solar cell, as explained above. The kinds of the transition metal oxide and lanthanide oxide are not specifically limited. Preferably, the transition metal oxide may be at least one selected from the group consisting of MnO , MnO_2 , Co_3O_4 , Co_2O_3 , CoO , TiO_2 , V_2O_5 and CuO . And, the lanthanide oxide may be at least one selected from the group consisting of CeO_2 , Pr_2O_3 , Eu_2O_3 , Tb_2O_3 , Nd_2O_3 and Sm_2O_3 . The (c) transition metal oxide, lanthanide oxide or a mixture thereof may be included in the residual content of 100 wt% of total glass frit composition, and preferably it may be included in the content of 0.1 to 20 wt% based on total glass frit composition. If the content is less than 0.1 wt%, the function for forming a p^{++} layer may be deteriorated, and if it exceeds 20 wt%,

contents of other ingredients may be relatively decreased rendering glass formation difficult.

Further, the glass frit composition of the present invention essentially comprises (d) P_2O_5 and (e) BaO for stable structure of the glass and to prevent moisture reactivity and improve electrical property. Namely, by using the P_2O_5 and BaO, moisture stability of an aluminum fired film may be increased to prevent discoloration when moisture penetrates, and adhesion between the substrate and the fired film may be maintained to prevent picking of the fired film. If one of the two ingredients is not included, glass having excellent bowing and capable of controlling reactivity with moisture may not be obtained.

Preferably, the glass frit composition comprises (d) P_2O_5 in the content of 3 to 5 wt% based on total glass frit composition. Specifically, if the content of P_2O_5 is 3 to 5 wt%, thermal property matching the firing temperature of aluminum powder may be effectively embodied, and if the content exceeds or less than the above range, moisture stability may not be expected.

And, the glass frit composition comprises (e) BaO in the content of 3 to 5 wt% based on total glass frit composition. Specifically, if the content of BaO is 3 to 5 wt%, identical effect as obtained in the above P_2O_5 content range may be expected, and if the content exceeds or less than the above range, moisture stability may not be expected.

Therefore, even if the existing glass frit composition comprises P_2O_5 and BaO, it is not included in the specific content ranges of the present invention, and thus, the above problem of moisture stability improvement cannot be solved.

Specifically, although adding of P_2O_5 and BaO may increase electrical property of a solar cell, if the content respectively exceeds 5 wt%, electrical property of a solar cell may be deteriorated, and moisture reactivity of fired film by the reaction of aluminum powder particle

film ingredient and glass may be increased when firing the paste, thus deteriorating stability. And, if the content is respectively less than 3 wt%, electrical property improvement may be insignificant, and reactivity between the aluminum fired film and moisture may be increased to cause discoloration by moisture.

The glass frit composition of the present invention has an average particle size of 0.5 to 20 μm , moisture content of 5% or less, and coefficient of thermal expansion of $50 \times 10^{-7}/^{\circ}\text{C}$ to $150 \times 10^{-7}/^{\circ}\text{C}$. And, to control bowing of a substrate after firing, the average particle diameter of the glass frit may be preferably 0.5~10 μm . If the average particle diameter is less than 0.5 μm , bowing may become too large, and if it exceeds 10 μm , dispersion stability in the paste may be deteriorated. And, if the moisture content of the glass frit composition exceeds 5%, viscosity of the paste may increase due to cross-linking of moisture and organic substance.

And, the glass frit composition may preferably have a softening point (T_s) of 400 to 600 $^{\circ}\text{C}$ and glass transition temperature (T_g) of 350 to 550 $^{\circ}\text{C}$.

And, the glass frit composition of the present invention may further comprise Na_2O , if necessary. The Na_2O is used to compensate electrical property. The content may be 1 to 10%, preferably 3 to 9 wt%, based on total glass frit composition. If the Na_2O is added, the contents of above explained ingredients may be respectively controlled so as to satisfy 100 wt% of the composition within each range.

Preferably, the glass frit composition may have one composition selected from the group consisting of

$\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-CeO}_2\text{-CoO}$,

$\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2\text{-CoO-CeO}_2\text{-CuO}$,

$\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2\text{-CoO-CeO}_2$, $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2\text{-CuO}$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2$, $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Na}_2\text{O-CeO}_2$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Na}_2\text{O-CoO}$, $\text{ZnO-SiO}_2\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2\text{-CuO}$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Na}_2\text{O-MnO}_2\text{-CoO-CeO}_2$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Nd}_2\text{O}_3\text{-Co}_3\text{O}_4$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO-Co}_2\text{O}_3\text{-Tb}_2\text{O}_3\text{-CuO}$, and
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO-Co}_2\text{O}_3\text{-Pr}_2\text{O}_3$. More preferably, the glass frit
composition may have the composition of
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Na}_2\text{O-MnO}_2\text{-CoO-CeO}_2$ because it may improve electrical
property of a battery, have excellent moisture reaction stability, and largely reduce substrate
bowing thus being effective for preventing break.

The glass frit composition of the present invention may be prepared by a common method without specific limitation.

For example, glass powder may be prepared by mixing each ingredient for a sufficient time of about 2 hours so as to be completely mixed, melting, quenching and pulverizing.

The melting may be conducted at a temperature of from 1,000 to 1,500°C, preferably 1,300 to 1,450°C. And, the melting time may be 10 to 60 minutes such that the glass composition may be uniformly mixed in a molten state. If the melting temperature is less than 1,000°C, melt viscosity may be high and thus each ingredient may not be uniformly mixed.

The quenching is a rapid cooling of the glass composition molten in the melting step. One or both of dry and wet quenching may be conducted for the glass composition.

The pulverization is a step wherein the quenched glass melt is primarily crude

pulverized using a common pulverizer such as a ball mill, and secondarily repulverized to microparticles of desired size to prepare glass powder.

Meanwhile, the present invention provides an aluminum paste composition for forming back contact of a solar cell using the ZnO-based glass frit composition.

The aluminum paste composition is a lead-free composition comprising aluminum powder, an inorganic binder, and an organic vehicle, wherein the aluminum paste composition comprises the above explained ZnO-based glass frit composition as the inorganic binder.

The aluminum paste composition may comprise 40 to 90 wt% of aluminum powder, 0.1 to 10 wt% of the inorganic binder, and 1 to 50 wt% of the organic vehicle. The organic vehicle may be a mixture comprising 1 to 50 wt% of an organic binder, 45 to 95 wt% of an organic solvent, and 0.1 to 10 wt% of additives.

If the content of the aluminum powder is less than 40 wt%, compactness may be decreased to deteriorate electrical property, and if it exceeds 90 wt%, viscosity control may be difficult and paste preparation may be difficult. Particularly, if the content of the inorganic binder is less than 0.1 wt% in the aluminum paste composition, adhesion between the fired film and wafer may be decreased, and if it exceeds 10 wt%, a reaction between the aluminum of the glass and wafer may be inhibited when firing to deteriorate electrical property. And, if the content of the organic vehicle is less than 1 wt%, it may be difficult to embody rheology property of the paste as the case wherein the content of the aluminum powder exceeds 90 wt%, and if it exceeds 50 wt%, pores may be increased when firing to deteriorate electrical property.

As explained, in the aluminum paste composition of the present invention, the ZnO-based glass frit of the present invention may be used alone as the inorganic binder, and

when the content is 10 wt% or less, bowing may be further improved. And, if necessary, Bi_2O_3 -based glass frit and ZnO-based glass frit may be mixedly used as the inorganic binder.

And, in the present invention, each ingredient used in the aluminum paste composition may be any material well known to a person having ordinary knowledge in the art, except the ZnO-based glass frit.

For example, the aluminum powder may be spherical, non-spherical or flake-shaped, and have purity of 80% or more and an average particle size of 1 to 30 micron, preferably 1 to 20 micron. The aluminum powder may include at least one selected from the ingredients corresponding to Ag, B, Ga, In, Tl and Si.

The organic binder may include cellulose derivatives such as methyl cellulose, ethyl cellulose, nitro cellulose, or hydroxyl cellulose; acrylic resin; alkyd resin; polypropylene based resin; polyvinyl chloride based resin; polyurethane based resin; epoxy based resin; silicone based resin; rosin based resin; terpene based resin; phenol based resin; aliphatic petroleum resin; acrylic ester based resin; xylene based resin; coumarone inden based resin; styrene based resin; dicyclopentadiene based resin; polybutene based resin; polyether based resin; urea based resin; melamine based resin; vinyl acetate based resin; polyisobutyl based resin, and a combination thereof.

The organic solvent may include butylcarbitol acetate, butylcarbitol, propyleneglycol monomethylether, dipropyleneglycol monomethylether, propyleneglycol monomethylether propionate, ethylether propionate, propyleneglycol monomethylether acetate, terpenol, texanol, dimethylamino formaldehyde, methyl ethyl ketone, gammabutyrolactone, ethyl lactate, and a combination thereof.

The additives may include fatty acids for improving wettability and flowability such as oleic acid, maleic acid, palmitic acid, myristic acid, lauric acid, stearic acid; an antifoaming agent for reducing foams, a dispersant for improving dispersibility, a plasticizer for controlling solubility of the organic binder, and the like, and a combination thereof. If the additive is used alone, the content may be 0.1 to 10 wt%. And, if a mixture of 2 or more kinds of the additives is used, the 2 or more kinds of ingredients may be appropriately mixed such that the content of the mixture may fall within the range of 0.1 to 10 wt%.

Meanwhile, the present invention provides back contact of a solar cell manufactured using the lead-free aluminum paste composition. The solar cell may be a silicon solar cell.

The method of manufacturing the back contact of a solar cell is obvious to one of ordinary knowledge in the art, and the detailed description is skipped.

For example, the aluminum paste composition may be printed on a substrate by a common method such as screen printing, doctor blade, inkjet printing, gravure printing, and the like, dried, and fired to form back contact. The substrate may include any silicon substrate used for front contact of a silicon solar cell without specific limitation. And, the drying may be progressed at a temperature of from 150 to 350 °C for 1 to 30 minutes, and the firing may be progressed under temperature condition of a maximum temperature of from 750 to 950 °C for a several seconds to 5 minutes.

By the above method, a solar cell having back contact of a thickness of 20 to 40um may be manufactured, and the formed back contact has good adhesion to a substrate, and equal or better mechanical strength compared existing back contact, and it may minimize substrate bowing and break due to shrinkage difference at cooling after firing the substrate by using the

ZnO-based glass frit composition having low coefficient of thermal expansion.

Accordingly, the present invention may manufacture a silicon solar cell with excellent performance, having front contact, an emitter layer, and an anti-reflection layer, and the like, using the back contact.

According to the present invention, since back contact of a solar cell is formed using a ZnO-based glass frit composition with a specific composition having low coefficient of thermal expansion, open circuit voltage may be improved by voltage increase of upper and lower ends of the substrate of the solar cell, thus improving photoconversion efficiency, and particularly, largely reducing bowing of the substrate. And, since the ZnO-based glass frit composition of the present invention does not use an expensive bismuth-based compound having high coefficient of thermal expansion, it may contribute to cost reduction as well as efficiency improvement. Moreover, stability to moisture reactivity of the substrate may be improved to prevent discoloration of a fired film and prevent picking of an aluminum fired film.

Hereinafter, the present invention will be explained with reference to the following Examples and Comparative Examples. However, these examples are only to illustrate the invention, and the present invention is not limited thereto.

Comparative Examples 1 to 6 and Examples 1 to 8

Metal oxides were mixed by the following method so as to have the composition as described in the following Table 1, to prepare a glass frit composition (unit: wt%).

Specifically, raw materials corresponding to the composition of the Table 1 were completely mixed for a sufficient time of 2hr using a non-gravity mixer (SONGYOUNGTECH CO., LTD. DC200W (experimental mixer)). And then, the mixture was molten at 1500°C for 30 minutes.

Subsequently, the molten glass composition was quenched to rapidly cool. For this, the glass composition was moved from the melting furnace through a transfer belt, taken out of the melting furnace, of which temperature is room temperature, within 10 seconds to rapidly cool, and maintained for 30 minutes to stabilize. The rapidly cooled glass melt was subjected to primary crude pulverization process through a ball mill, and secondarily repulverized to a desired microparticle size, thus preparing glass powder.

After preparing glass powder, T_g, T_s, and CTE (coefficient of thermal expansion) of each composition were measured, and the results are described in the following Table 2.

[Table 1]

	Bi ₂ O ₃	ZnO	SiO ₂	B ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	BaO	Na ₂ O	MnO ₂	CeO ₂	CoO	CuO
Comparative Example1	60.6	7.2	6.5	4.6	6.2		8.1	6.8				
Comparative Example2		53.2	8.5	9.1	9.3			1.5	10.1			8.3
Comparative Example3		50.1	10.9	15	3.9	11.8	8.3					
Comparative Example4		54.2	10.4	12.6	7.3		4.2	1.9	5.8			3.6
Comparative Example5		48.7	9.6	9.8	7.9	4.6	0.9	1.9		9.7	6.9	

Comparative Example 6		51	13.7	10.9	9.1	4.1			5.2		2.7	3.3
Example 1		52.4	9.3	11.5	7.2	3.6	4.4			6.1	5.5	
Example 2		49.9	9.4	12.5		4.2	4.1		6.4	5.9	3.7	3.9
Example 3		47.3	6.6	12.9	5.7	3.5	4.9	3.5	3.6	6.9	5.1	
Example 4		51	13.7	10.9		4.1	4.8		12.2			3.3
Example 5		52.7	17.3	16.5		4.2	3.1		6.2			
Example 6		54.7	15.2	4.9	8.2	4.5	4.7	6.6		1.2		
Example 7		54.9	10.9	15		3.4	5	8.9			1.9	
Example 8		53.2	8.5		9.3	4.7	4.9	3.9	7.1			8.4

[Table 2]

	Tg(°C)	Ts(°C)	CTE ($\times 10^{-7}/^{\circ}\text{C}$)
Comparative Example 1	531	539	102
Comparative Example 2	495	527	98
Comparative Example 3	473	509	85
Comparative Example 4	460	503	95
Comparative Example 5	485	510	85
Comparative Example 6	488	512	92
Example 1	480	512	78

Example 2	431	475	76
Example 3	492	507	73
Example 4	471	511	77
Example 5	466	509	76
Example 6	468	507	76
Example 7	470	511	75
Example 8	471	508	74

From the results of Table 2, it is confirmed that Examples 1 to 8 of the present invention have low coefficient of thermal expansion compared to Comparative Examples 1 to 6, thus preventing bowing of the substrate after firing.

Comparative Example 7 to 12 and Example 9 to 16

With the compositions and compositional ratios of the following Tables 3, 4 and 5, each aluminum paste of Comparative Examples and Examples was prepared using glass frit, aluminum powder and an organic vehicle (unit: wt%). Wherein, aluminum powder having average particle diameter of 3 micron was used, and for the organic vehicle, ethylcellulose was used as the organic binder, butylcarbitolacetate was used as the organic solvent, and oleic acid and dispersant (disperbyk-183 1.5%) were used as additives. And then, moisture reaction stability was evaluated, and photoconversion property was measured by a common method.

And, moisture reaction stability of Comparative Example 8 and Example 11 were

evaluated and the results are shown in Fig. 1, and bowing of Comparative Example 7 and Example 11 were evaluated and the results are shown in Fig. 2.

The moisture reaction stability was evaluated as follow.

DI water was filled in a beaker and maintained in an oven or a hot plate at 70°C. A fired wafer was impregnated in a temperature-maintained beaker for 10 minutes and it was confirmed whether or not bubbles are generated. And, the wafer taken out of the beaker was completely dried, and film adhesion was confirmed by taping test (if moisture reaction stability is low, picking of the film occurs). The evaluation standard is as follow.

○: No bubble generation and no picking of fired film

△: Bubble generation or picking of fired film

×: Serious bubble generation and picking of fired film

[Table 3]

	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12
Cellulose resin	4	4	4	4	4	4
Organic solvent	14.5	14.5	14.5	14.5	14.5	14.5
Additives	1.5	1.5	1.5	1.5	1.5	1.5
Glass frit	5	5	5	5	5	5
	(Comparative Example 1)	(Comparative Example 2)	(Comparative Example 3)	(Comparative Example 4)	(Comparative Example 5)	(Comparative Example 6)
aluminum powder	75	75	75	75	75	75
Voc (V)	0.619	0.623	0.618	0.619	0.619	0.62
Eff (%)	16.75	16.9	16.71	16.8	16.81	16.84

Bowing at 180um thickness	1.34	1.51	1.21	1.42	1.38	1.44
Bowing at 200um thickness	1.10	1.29	0.99	1.12	1.08	1.18
Moisture reaction stability	○	×	×	△	△	△

[Table 4]

	Example 9	Example 10	Example 11	Example 12
Cellulose resin	4	4	4	4
Organic solvent	14.5	14.5	14.5	14.5
Additives	1.5	1.5	1.5	1.5
Glass frit	5	5	5	5
	(Example 1)	(Example 2)	(Example 3)	(Example 4)
Aluminum powder	75	75	75	75
Voc (V)	0.625	0.625	0.626	0.625
Eff (%)	17	16.99	17.08	16.95
Bowing at 180um thickness	1.05	0.98	0.88	0.99
Bowing at 200um thickness	0.7	0.66	0.64	0.65
Moisture reaction stability	○	○	○	○

[Table 5]

	Example 13	Example 14	Example 15	Example 16
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Cellulose resin	4	4	4	4
Organic solvent	14.5	14.5	14.5	14.5
Additives	1.5	1.5	1.5	1.5
Glass frit	5	5	5	5
	(Example 5)	(Example 6)	(Example 7)	(Example 8)
Aluminum powder	75	75	75	75
Voc (V)	0.624	0.624	0.624	0.625
Eff (%)	16.92	16.91	16.92	17.03
Bowing (at 180um thickness)	0.93	1.01	1	0.97
Bowing (at 200um thickness)	0.69	0.67	0.66	0.67
Moisture reaction stability	○	○	○	○

As shown in the Tables 3 to 5, Examples 9 to 16 of the present invention using glass frit of specific composition exhibit increased open circuit voltage and more excellent photoconversion efficiency compared to Comparative Example 7, Comparative Example 9 using glass frit that does not contain transition metal oxide (Comparative Example 1, Comparative Example 3).

And, Examples 9 to 16 of the present invention minimize break due to small bowing of the substrate, and exhibit excellent moisture reaction stability of the fired film.

To the contrary, Comparative Examples 7 to 12 generally exhibit inferior electrical property, moisture stability and bowing. As shown in Fig. 1, although Comparative Example 7 is

stable to moisture reaction, it should use a bismuth-based compound, and the substrate may be broken due to high bowing. And, Comparative Examples 9 to 12 exhibit bad electrical property and moisture reaction stability and high bowing compared to Example 11. And, as shown in Fig. 2, Comparative Examples 8, 9 exhibit inferior moisture reaction stability compared to Example 11, and picking of the fired film of the substrate occurs.

Examples 17 to 22

To further evaluate optimum glass composition of the wafer, an aluminum paste was prepared with the compositions and compositional ratios as described in the following Table 6, using the glass frit of Example 3 having most excellent bowing (unit: wt%). And, the same aluminum powder, organic binder, organic solvent and additives as the Examples 9 to 16 were used.

[Table 6]

	Example17	Example18	Example19	Example20	Example21	Example22
Cellulose resin	4	4	4	4	4	4
Organic solvent	16.5	16	15.5	15	14.5	14
Additives	1.5	1.5	1.5	1.5	1.5	1.5
Glass frit	3 (Example3)	3.5 (Example3)	4 (Example3)	4.5 (Example3)	5 (Example3)	5.5 (Example3)
Aluminum powder	75	75	75	75	75	75
Voc (V)	0.628	0.627	0.627	0.626	0.626	0.625
Eff (%)	17.2	17.15	17.09	17.08	17.08	17.05

Bowing (at 200um thickness)	0.54	0.59	0.59	0.6	0.64	0.97
Moisture reaction stability	○	○	○	○	○	○

As shown in the Table 6, although Examples 17 to 22 using the glass frit of Example 3 of the present invention exhibit deteriorated electrical property and bowing as the content of glass frit increases, they exhibit excellent properties compared to Comparative Examples.

WHAT IS CLAIMED IS

1. A glass frit composition for forming an aluminum paste for back contact of a solar cell comprising:

- (a) 45 to 60 wt% of ZnO,
- (b) at least one metal oxide selected from the group consisting of 0.1 to 45 wt% of SiO₂, 0.1 to 40 wt% of B₂O₃, and 1 to 10 wt% of Al₂O₃,
- (c) 0.1 to 20 wt% of transition metal oxide, lanthanide oxide, or a mixture thereof,
- (d) 3 to 5 wt% of P₂O₅, and
- (e) 3 to 5 wt% of BaO.

2. The glass frit composition according to claim 1, wherein the glass frit composition has an average particle size of 0.5 to 20 μm , moisture content of 5% or less, and coefficient of thermal expansion of $50 \times 10^{-7}/^{\circ}\text{C}$ to $150 \times 10^{-7}/^{\circ}\text{C}$.

3. The glass frit composition according to claim 1, wherein the glass frit composition further comprises 1 to 10 wt% of Na₂O, based on total glass frit composition.

4. The glass frit composition according to claim 1, wherein the transition metal oxide is at least one selected from the group consisting of MnO, MnO₂, Co₃O₄, Co₂O₃, CoO, TiO₂, V₂O₅ and CuO, and

wherein the lanthanide oxide is at least one selected from the group consisting of CeO₂, Pr₂O₃, Eu₂O₃, Tb₂O₃, Nd₂O₃ and Sm₂O₃.

5. The glass frit composition according to claim 1, wherein the glass frit composition includes at least one selected from the group consisting of

$\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-CeO}_2\text{-CoO}$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2\text{-CoO-CeO}_2\text{-CuO}$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2\text{-CoO-CeO}_2$, $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2\text{-CuO}$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2$, $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Na}_2\text{O-CeO}_2$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Na}_2\text{O-CoO}$, $\text{ZnO-SiO}_2\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO}_2\text{-CuO}$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Na}_2\text{O-MnO}_2\text{-CoO-CeO}_2$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-Nd}_2\text{O}_3\text{-Co}_3\text{O}_4$,
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO-Co}_2\text{O}_3\text{-Tb}_2\text{O}_3\text{-CuO}$, and
 $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-BaO-P}_2\text{O}_5\text{-MnO-Co}_2\text{O}_3\text{-Pr}_2\text{O}_3$.

6. A lead-free aluminum paste composition for forming back contact of a solar cell comprising aluminum powder, an inorganic binder and an organic vehicle,

wherein the aluminum paste composition includes the ZnO-based glass frit composition according to any one of claims 1 to 5 as the inorganic binder.

7. The lead-free aluminum paste composition for forming back contact of a solar cell according to claim 6, wherein the aluminum paste composition comprises 40 to 90 wt% of the aluminum powder, 0.1 to 10 wt% of the inorganic binder, and 1 to 50 wt% of the organic vehicle.

8. The lead-free aluminum paste composition for forming back contact of a solar cell according to claim 7, wherein the organic vehicle is a mixture comprising 1 to 50 wt% of an organic binder, 45 to 95 wt% of an organic solvent, and 0.1 to 10 wt% of additives.

9. The lead-free aluminum paste composition for forming back contact of a solar cell according to claim 6, wherein the glass frit composition is at least one selected from the

group consisting of

ZnO-SiO₂-B₂O₃-Al₂O₃-BaO-P₂O₅-CeO₂-CoO,

ZnO-SiO₂-B₂O₃-BaO-P₂O₅-MnO₂-CoO-CeO₂-CuO,

ZnO-SiO₂-B₂O₃-Al₂O₃-BaO-P₂O₅-MnO₂-CoO-CeO₂, ZnO-SiO₂-B₂O₃-BaO-P₂O₅-MnO₂-CuO,

ZnO-SiO₂-B₂O₃-BaO-P₂O₅-MnO₂, ZnO-SiO₂-B₂O₃-Al₂O₃-BaO-P₂O₅-Na₂O-CeO₂,

ZnO-SiO₂-B₂O₃-BaO-P₂O₅-Na₂O-CoO, ZnO-SiO₂-Al₂O₃-BaO-P₂O₅-MnO₂-CuO,

ZnO-SiO₂-B₂O₃-Al₂O₃-BaO-P₂O₅-Na₂O-MnO₂-CoO-CeO₂,

ZnO-SiO₂-B₂O₃-Al₂O₃-BaO-P₂O₅-Nd₂O₃-Co₃O₄,

ZnO-SiO₂-B₂O₃-BaO-P₂O₅-MnO-Co₂O₃-Tb₂O₃-CuO, and

ZnO-SiO₂-B₂O₃-Al₂O₃-BaO-P₂O₅-MnO-Co₂O₃-Pr₂O₃.

10. The lead-free aluminum paste composition for forming back contact of a solar cell according to claim 8, wherein the organic binder is at least one selected from the group consisting of cellulose derivatives selected from methyl cellulose, ethyl cellulose, nitro cellulose, or hydroxyl cellulose; acrylic resin; alkyd resin; polypropylene based resin; polyvinyl chloride based resin; polyurethane based resin; epoxy based resin; silicone based resin; rosin based resin; terpene based resin; phenol based resin; aliphatic petroleum resin; acrylic ester based resin; xylene based resin; coumarone inden based resin; styrene based resin; dicyclopentadiene based resin; polybutene based resin; polyether based resin; urea based resin; melamine based resin; vinyl acetate based resin; and polyisobutyl based resin.

11. The lead-free aluminum paste composition for forming back contact of a solar cell according to claim 8, wherein the organic solvent is at least one selected from the group consisting of butylcarbitol acetate, butylcarbitol, propyleneglycol monomethylether,

dipropyleneglycol monomethylether, propyleneglycol monomethylether propionate, ethylether propionate, propyleneglycol monomethylether acetate, terpenol, texanol, dimethylamino formaldehyde, methyl ethyl ketone, gammabutyrolactone, and ethyl lactate.

12. The lead-free aluminum paste composition for forming back contact of a solar cell according to claim 6, wherein the aluminum powder is spherical, non-spherical or flake-shaped, has a purity of 80% or more and an average particle size of 1 to 30 micron, and includes at least one selected from Ag, B, Ga, In, Tl and Si.

13. The lead-free aluminum paste composition for forming back contact of a solar cell according to claim 8, wherein the additive is at least one selected from the group consisting of oleic acid, maleic acid, palmitic acid, myristic acid, lauric acid, stearic acid, an antifoaming agent, a dispersant, and a plasticizer.

14. A back contact for a solar cell manufactured using the lead-free aluminum paste composition according to claim 6.

FIG. 1

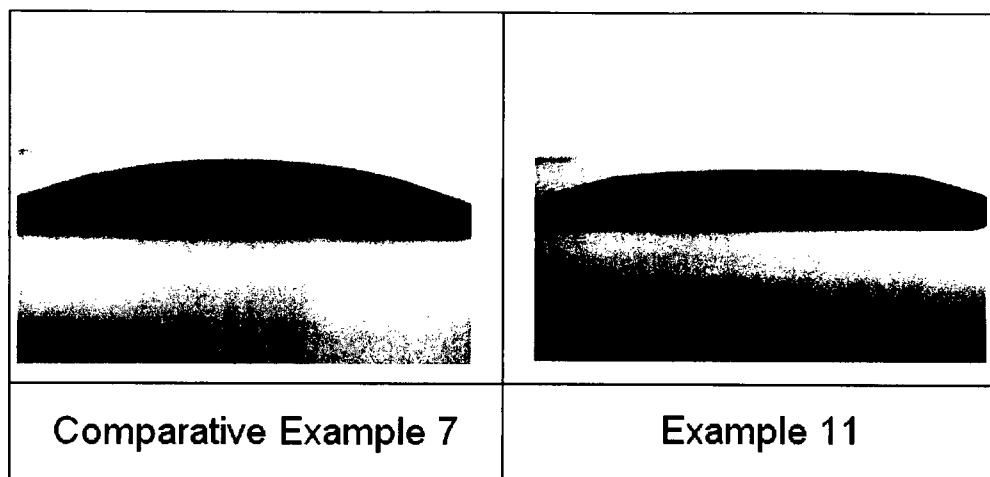


FIG. 2

