(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
9 June 2016 (09.06.2016)

WIPO | PCT

(10) **International Publication Number**
WO 2016/087252 A1

(51) International Patent Classification:
C03C 17/00 (2006.01) ***H01L 51/00*** (2006.01) ***C03C 17/04*** (2006.01) ***H01L 51/52*** (2006.01) ***C03C 17/34*** (2006.01) ***C03C 21/00*** (2006.01) ***C03C 8/04*** (2006.01)

(21) International Application Number:
PCT/EP2015/077393

(22) International Filing Date:
23 November 2015 (23.11.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
14195677.1 1 December 2014 (01.12.2014) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,

[Continued on next page]

(54) Title: TRANSPARENT DIFFUSIVE OLED SUBSTRATE AND METHOD FOR PRODUCING SUCH A SUBSTRATE

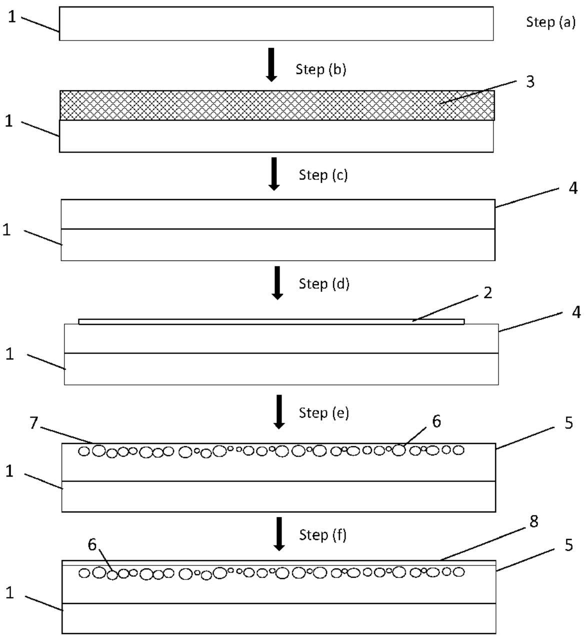


Figure 1

(57) Abstract: The invention is drawn to a method for preparing a laminate substrate for a light emitting device, said method comprising the following successive steps: (a) providing a glass substrate (1) having a refraction index, at 550 nm, of between 1.45 and 1.65, (b) coating a glass frit (3) comprising at least 30 weight % of Bi_2O_3 and having a refractive index, at 550 nm, of at least 1.7 onto said glass substrate (1), (c) firing the resulting frit coated glass substrate at a temperature above the Littleton temperature of the glass frit thereby forming a first high index enamel layer (4), (d) coating a metal oxide layer (2) onto said first high index enamel layer, (e) firing the resulting coated glass substrate at a temperature above the Littleton temperature of the glass frit, comprised between 530 °C and 620 °C, thereby making react the metal oxide (2) with the underlying first high index enamel layer (4) and forming a second high index enamel layer (5) with a plurality of spherical voids (6) embedded in the upper section of the second high index enamel layer (5) near the interface with air, and optionally (f) coating a transparent electro-conductive layer (TCL) (8) on the second high index enamel layer (5).

WO 2016/087252 A1

SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

TRANSPARENT DIFFUSIVE OLED SUBSTRATE AND METHOD FOR PRODUCING SUCH A SUBSTRATE

The present invention is drawn to a new method for producing translucent, light-scattering glass substrates for organic light emitting diodes (OLEDs) and to substrates obtainable by such a method.

OLEDs are opto-electronic elements comprising a stack of organic layers with fluorescent or phosphorescent dyes sandwiched between two electrodes, at least one of which is translucent. When a voltage is applied to the electrodes the electrons injected from the cathode and the holes injected from the anode combine within the organic layers, resulting in light emission from the fluorescent/phosphorescent layers.

It is commonly known that light extraction from conventional OLEDs is rather poor, most of the light being trapped by total internal reflection in the high index organic layers and transparent conductive layers (TCL). Total internal reflection takes place not only at the boundary between the high index TCL and the underlying glass substrate (refractive index of about 1.5) but also at the boundary between the glass and the air.

According to estimates, in conventional OLEDs not comprising any additional extraction layer about 60 % of the light emitted from the organic layers is trapped at the TCL/glass boundary, an additional 20 % fraction is trapped at the glass/air surface and only about 20 % exit the OLED into air.

It is known to reduce this light entrapment by means of a light scattering layer between the TCL and the glass substrate. Such light scattering layers have a transparent matrix with a high refractive index close to the TCL refractive index and contain à plurality of light scattering elements having a refractive index different from that of the matrix. Such high index matrices are commonly obtained by fusing a high index glass frit thereby obtaining thin high index enamel layers on low index glass substrates. The light scattering elements may be solid particles added to the glass frit before the fusing step, crystals formed during the fusing step or air bubbles formed during the fusing step.

It is also known to increase out-coupling of light by texturing the interface, i.e. creating a relief at the interface between the glass and the high index layers of the OLED, for example by etching or lapping of the low index transparent substrate before applying and fusing a high index glass frit.

Both of these extraction means are commonly called “internal extraction layers” (IEL) because they are located between the OLED substrate and the TCL.

External extraction layers (EEL), also commonly known in the art, work in a similar way but are located at the glass/air boundary.

The present invention is in the field of internal extraction layers (IEL) having a transparent high index glass matrix containing air bubbles as low index diffusing elements. Such IEL with light diffusing air bubbles are advantageous over similar IEL with solid particles because there is no risk of large sized particles protruding from the matrix and generating short-circuits and/or inter-electrode leakage currents in the final OLED product.

In spite of the absence of solid particles it is however not easy to obtain diffusing enamels with a perfect surface quality by simply fusing high index glass frits on low index glass substrates. As a matter of fact the air bubbles formed and entrapped in the melting matrix during the fusing step rise towards the surface where they burst and level out. However, open or partially open air bubbles, solidified at the IEL surface before completely leveling out create crater-like surface irregularities that may have rather sharps edges and lead to inter-electrode leakage currents and pin-holes in the final OLED.

EP 2 178 343 B1 discloses a translucent glass substrate for OLEDs with an internal extraction layer (scattering layer) comprising a high index glass matrix and air bubble scattering elements. According to this document, the surface of the scattering layer is free of surface defects due to open air bubble craters (see [0026] to [0028], and Fig 55). A thorough analysis of this document and in particular of [0202] shows however that this result is simply an artifact due to an inappropriate method of counting the scattering elements in the lower surface layers.

The Applicant has recently filed a South Korean patent application No 10-2013-0084314 (July 17, 2013), not published on the filing date of the present application, disclosing a laminate substrate for a light emitting device with a system of highly interconnected voids located at the interface between the low index glass substrate and the high index enamel. Such a scattering layer has a very high surface quality with an open bubble density of less than $0.1/cm^2$, but suffers from the inconvenience that water or other fluids coming into contact with the edges of the laminate substrate may percolate through the interconnected voids over large areas of the laminate and, through pinholes, into the stack of organic layers with fluorescent or phosphorescent dyes, resulting in destruction of said layers.

It would therefore be advantageous to provide a laminate substrate for OLEDs similar to the one described in South Korean application No 10-2013-0084314 filed on July 17, 2013 in the name of Saint-Gobain Glass France where the interconnected void system at the high index enamel/glass substrate layer is replaced by a plurality of individual air bubbles not connected to each other and sticking to said interface, essentially without rising to the surface of the melting high index glass frit.

The Applicant surprisingly found that a high number of individual air bubbles formed in the lower layer of a melting high index frit, sticking to the underlying glass substrate essentially without rising to the surface, when the glass frit was applied and fused not directly in contact with the glass substrate but on a thin metal oxide layer previously coated onto said glass surface beforehand. A European patent application (EP 14177291.3) regarding such a method and product has recently been filed but not been published before the filing of the present application.

The Applicant has now surprisingly found an alternative method where a thin metal oxide layer is coated *on top* of a high index enamel layer – and not, as in EP14177291.3, *under* said enamel layer. The coated substrate/enamel/metal oxide laminate is then fired at about 570 °C. Upon firing components of the top metal oxide layer react with components of the underlying enamel forming a thin surface layer with a plurality of spherical voids entrapped therein. It was rather surprising to note that the spherical voids, in spite of being so near to the surface of the fired layer, advantageously did not rise to burst at the surface. Open or partially open bubbles, solidified at the surface before completely leveling out would indeed create crater-like surface irregularities that may have rather sharp edges and lead to inter-electrode leakage currents and pin-holes in the final OLED. The rather surprising fact that the voids, forming in the upper surface layer of the high index enamel, do not rise to the surface thereof consequently guarantees excellent surface quality and prevents leakage currents in the final OLED.

Moreover it has been shown (see Fig 4) that coating and firing of such a thin metal oxide layer on a high index enamel layer allowed healing, or curing, of preexisting open bubble surface defects.

The subject-matter of the present application is a method for preparing a laminate substrate for a light emitting device, comprising at least the following five steps:

(a) providing a glass substrate having a refraction index (at $\lambda = 550$ nm) of between 1.45 and 1.65,

(b) coating a glass frit having a refractive index (at $\lambda = 550$ nm) of at least 1.7 onto said glass substrate,

(c) firing the frit-coated glass substrate at a temperature above the Littleton temperature of the glass frit, thereby forming a first high index enamel layer,

(d) coating a metal oxide layer onto said first high index enamel layer, and

(e) firing the resulting coated glass substrate at a temperature above the Littleton temperature of the glass frit thereby making react the metal oxide with the underlying first high index enamel layer and forming a second high index enamel layer with a plurality of spherical voids embedded in the upper section of the second enamel layer near the interface with air.

Another subject-matter of the present application is a laminate substrate obtainable by the above method, said laminate comprising

(i) a glass substrate having a refractive index of between 1.45 and 1.65,

(ii) a high index glass enamel layer having a refractive index (at 550 nm) of at least 1.7,

characterized by the fact that a plurality of spherical voids are embedded in the high index enamel layer near the surface thereof, at least 95 %, preferably at least 99 %, and more preferably essentially all of the spherical voids having a diameter significantly smaller than the half-thickness of the enamel layer and being located in the upper half of the high index enamel layer near the interface with air.

The glass substrate provided in step (a) is a flat translucent or transparent substrate of mineral glass, for example soda lime glass, generally having a thickness of between 0.1 and 5 mm, preferably of between 0.3 and 1.6 mm. Its light transmission (ISO9050 standard, illuminant D65 (TLD) such as defined by ISO/IEC 10526 standard in considering the standard colorimetric observer CIE 1931 as defined by the ISO / IEC 10527) preferably is as high as possible and typically higher than 80 %, preferably higher than 85 % or even higher than 90 %.

In step (b) of the method of the present invention a glass frit having a refractive index, at $\lambda = 550$ nm, of at least 1.7 is coated onto the glass substrate. The refractive index of said glass frit is preferably comprised between 1.70 and 2.20, more preferably between 1.80 and 2.10.

The high index glass frit advantageously comprises at least 30 weight %, preferably at least 50 weight % and more preferably at least 60 weight % of Bi_2O_3.

The glass frit should be selected to have a melting point (Littleton point) comprised between 450 °C and 570 °C and should lead to an enamel having a refractive index of 1.8 to 2.1.

Preferred glass frits have the following composition:

Bi_2O_3: 55 – 75 wt%
BaO: 0 – 20 wt%
ZnO: 0 – 20 wt%
Al_2O_3: 1 – 7 wt%
SiO_2: 5 – 15 wt%
B_2O_3: 5 – 20 wt%
Na_2O: 0.1 – 1 wt%

CeO_2: 0 – 0.1 wt%

In a typical embodiment, the glass frit particles (70 – 80 wt%) are mixed with 20 – 30 wt% of an organic vehicle (ethyl cellulose and organic solvent). The resulting frit paste is then applied onto the glass substrate by screen printing or slot die coating. The resulting layer is dried by heating at a temperature of 120 – 200 °C. The organic binder (ethyl cellulose) is burned out at a temperature of between 350 – 440 °C.

The amount of the high index glass frit coated onto the glass substrate is generally comprised between 20 and 200 g/m^2, preferably between 25 and 150 g/m^2, more preferably between 30 and 100 g/m^2, and most preferably between 35 and 70 g/m^2.

The frit-coated glass substrate is then submitted to a first firing step (step (c)) where the glass frit is heated to a temperature above the Littleton temperature of the glass frit, resulting in fusion of the glass frit and formation of a first high index enamel layer. This firing step, i.e. the fusing of the high index glass frit, resulting in the first high index enamel layer is preferably carried out at a temperature of between 530 °C and 620 °C, more preferably between 540 °C and 600 °C

In the next step (step (d)) of the method of the present invention, a thin layer of a metal oxide is coated by any suitable method onto the first high index enamel layer, preferably by reactive or non-reactive magnetron sputtering, chemical vapor deposition (CVD), atomic layer deposition (ALD) or sol-gel wet coating. Said metal oxide layer may cover the whole surface of the first enamel layer. In an alternative embodiment, only part of the surface of the first enamel layer is coated with the metal oxide layer. It could be particularly interesting to coat the substrate with a patterned metal oxide layer in order to prepare a final laminate substrate with a non-uniform extraction pattern.

After coating of the metal oxide layer, the resulting coated glass substrate is submitted to a second firing step (step (e))

Without wanting to be bound by any theory, the Applicant thinks that the light scattering spherical voids are generated during the firing step (e) by reaction between the metal oxide and a component of the underlying first high index enamel layer. The specific nature of said reaction has not yet been fully elucidated. It is thought that O_2 gas could evolve as a reaction product. The majority of the spherical voids are not just air bubbles entrapped in the glass frit during the fusion-solidification steps, such as described in EP 2 178 343 B1, but gas bubbles generated during the firing step.

As a matter of fact, the Applicant observed that the density of spherical voids is far higher in areas where the first enamel layer is coated with the metal oxide layer than in areas where it is not.

There is no specific lower limit to the thickness of the metal oxide layer as long as it provides enough reactive components for generating a significant amount of spherical voids in the upper half of the second high index enamel layer. A metal oxide layer of a few nanometers only has turned out to be able to trigger the formation of the desirable spherical voids. The metal oxide layer should preferably be thin enough for completely breaking down during the second firing step by reacting with the underlying high index enamel.

The metal oxide layer preferably has a thickness of between 5 and 60 nm, more preferably of between 10 and 40 nm, and even more preferably of between 15 and 30 nm.

At the time the present application was filed, the Applicant had experimentally shown that at least three metal oxides, i.e. TiO_2, Al_2O_3, ZrO_2, led to formation of said spherical voids. The skilled person, without departing from the spirit of the present invention, may easily replace these metal oxides by different metal oxides such as, Nb_2O_5, HfO_2, Ta_2O_5, WO_3, Ga_2O_3, In_2O_3 and SnO_2, or mixtures thereof in order to complete the experimental work of the Applicant and find additional metal oxides suitable for use in the method of the present invention.

The metal oxide consequently is preferably selected from the group consisting of TiO_2, Al_2O_3, ZrO_2, Nb_2O_5, HfO_2, Ta_2O_5, WO_3, Ga_2O_3, In_2O_3, SnO_2, and mixtures thereof.

In the firing step (e) the substrate is again heated to a temperature above the Littleton temperature of the glass frit, resulting in reaction of components of the metal oxide with components of the underlying high index enamel layer, and formation of spherical voids in this reaction zone. In the final solidified enamel coating, it is generally impossible to clearly differentiate the original metal oxide layer from the glass frit layer. Most probably the metal oxide layer is digested by the first enamel layer creating locally a melting enamel with a slightly different composition. It is therefore impossible to specify the thickness of each of these two layers in the final laminate.

The overall thickness of the solidified enamel layer, called “second high index enamel layer” comprising a plurality of spherical voids (scattering elements) embedded therein is preferably comprised between 3 µm and 25 µm, more preferably between 4 µm and 20 µm and most preferably between 5 µm and 15 µm.

One of the most surprising aspects of the present invention is the observation that the gaseous bubbles formed during the second firing step (step (e)) do not rise in the molten glass phase towards the surface thereof but seem to be held back at a location slightly below the interface with atmosphere. This “holding down” of the scattering elements results in an excellent surface quality of the solidified high index enamel, without crater-like recesses due to solidified open bubbles.

To efficiently prevent the spherical voids from rising to the surface of the second high index enamel layer, the firing temperature of step (e) however should not be excessively high and the duration of the firing step should not be excessively long.

The duration of the firing step (e) is preferably comprised between 3 and 30 minutes, more preferably between 5 and 20 minutes. The firing temperature of step (e) should be comprised between 530 °C and 620 °C, more preferably between 540 °C and 600 °C. The firing temperature is selected in dependence of the Littleton temperature of the high index glass frit and is preferably about 40 to 80 °C above the Littleton temperature of the high index glass frit.

It goes without saying that the high index glass frit used in the present invention and the enamel resulting therefrom should preferably be substantially devoid of solid scattering particles such as crystalline SiO_2 or TiO_2 particles. Such particles are commonly used as scattering elements in internal extraction layers but require an additional planarization layer, thereby undesirably increasing the total thickness of the extraction layer.

As already explained above the spherical voids formed during the firing step are not randomly distributed throughout the thickness of the second high index enamel layer but are located predominantly in the “upper” half, i.e. near the interface of said enamel layer with air. To be completely embedded in the enamel layer, the spherical voids of course must be significantly smaller than the thickness of the enamel layer. At least 95 %, preferably at least 99 %, and more preferably essentially all of the spherical air voids have a diameter smaller than the half-thickness of the enamel layer and are located in the upper half of the high index enamel layer near the interface thereof with atmosphere. The expression “located in the upper half of the high index enamel layer” means that at least 80 % of the void’s volume is located above the median plane of the enamel layer.

The spherical voids preferably have an average equivalent spherical diameter of between 0.2 µm and 8 µm, more preferably of between 0.4 µm and 4 µm, and most preferably of between 0.5 µm and 3 µm.

The spherical voids are randomly distributed over the whole area corresponding to the surface previously coated with the metal oxide layer. To efficiently scatter the light emitted from the stack of organic layers containing fluorescent or phosphorescent dyes, the density of the spherical voids preferably is comprised between 10^4 and 25.10^6 per mm^2, more preferably between 10^5 and 5.10^6 per mm^2.

When viewed from a direction perpendicular to the general plane of the substrate (projection view), the spherical voids preferably occupy at least 20 %, more preferably at least 25 % of the surface and at most 80 % more preferably at most 70 % of the surface of the area previously covered by the metal oxide.

As can be seen on Figures 2 and 3, showing respectively a perspective and a section view of a laminate substrate according to the present invention, nearly all the spherical voids are randomly aligned in the upper third of the final enamel layer, thereby forming a sort of monolayer of individual voids “floating” under the surface without touching it. Said voids may be very close to each other or even in contact with each other but are not connected to each other. Percolation of fluids, such as water or other solvents in liquid or gaseous form, entering from the periphery of the laminate substrate of the invention is thus efficiently impeded. OLEDs made from the laminate substrate of the present invention therefore are much less sensitive to water or solvent than those made from the laminate substrates described in the South Korean patent application No 10-2013-0084314.

The laminate substrate of the present invention is meant to be used as a translucent substrate for the production of bottom emitting OLEDs. A bottom emitting OLED comprises a translucent substrate carrying a translucent electrode, generally the anode, and a light reflecting electrode, generally the cathode. Light emitted from the stack of light-emitting organic layers is either emitted directly via the translucent anode and substrate or first reflected by the cathode towards and through the translucent anode and substrate.

Before laminating the light emitting organic layer stack, a transparent conductive layer (electrode layer) must therefore be coated on top of the internal extraction layer. In a preferred embodiment the laminate substrate of the present invention consequently further comprises a transparent electro-conductive layer on the high index enamel layer, this electro-conductive layer preferably being directly in contact with the enamel layer or being coated onto an intermediate layer, for example a barrier layer or protection layer.

In a preferred embodiment, the method of the present invention therefore further comprises an additional step of coating a transparent electro-conductive layer (TCL) on the high index enamel layer. This layer preferably is a transparent conductive oxide such as ITO (indium tin oxide). Formation of such a TCL may be carried out according to conventional methods familiar to the skilled person, such as magnetron sputtering.

Figure 1 is a flowchart showing the process of preparing the laminate substrate of the present invention

Figure 2 is a Scanning Electronic Microscope (SEM) photograph showing a view of cross-section and top surface of the laminate substrate of the present invention after the firing step (e).

Figure 3 is a Scanning Electronic Microscope (SEM) photograph showing a cross-sectional view of a laminate substrate according to the invention.

Figure 4 shows four top views of laminate substrates with preexisting open-bubble surface defects, before and after curing by coating and firing of a thin metal oxide layer.

Figure 5 shows a top view and cross-sectional view of a laminate substrate prepared according to the below Example.

In Figure 1, a flat transparent glass substrate 1 is first provided in step (a). In step (b) a high index glass frit 3 is then coated onto one side of this substrate for example by screen printing a paste including the glass frit and an organic medium (polymer & organic solvent). In the next step (step (c)) the resulting glass frit-coated substrate is heated to a temperature sufficient to melt the frit into a continuous high index enamel layer 4. This first high index enamel layer 4 is then coated, for example by magnetron sputtering, with a metal oxide 2.

The resulting substrate carrying the metal oxide layer 2 on the first high index enamel layer 4 is then submitted to a second firing step (step (e)). During this final heating step, spherical voids 6 form from reaction between the metal oxide and the first high index enamel layer 4, resulting in a second high index enamel layer 5 incorporating, below its interface 7 with atmosphere, a row of fine spherical voids 6. The spherical voids are rather close to the surface of the second high index enamel layer 5 but do not rise to the surface of this layer. A transparent electro-conducting layer 6 is then coated, in step (f), onto the perfectly smooth surface of the second high index enamel layer 5.

On the SEM photograph of Figure 2 one can see both the row of small spherical voids below the surface of the enamel layer, and also the high surface quality of this enamel layer.

On the SEM photograph of Figure 3 the black glass substrate is covered by a lighter grey layer of high index enamel, corresponding to the second high index layer 5 of Figure 1. A monolayer of spherical voids of different sizes is completely embedded therein and located close to but clearly below the interface with air (upper black coloured zone).

The laminate substrate shown does not yet comprise a transparent electro-conducting layer. One can see that the surface of the high index enamel layer is perfectly smooth and free of crater-like surface irregularities.

At figure 4 one can see at the first line two surface defects resulting from solidified burst bubbles in the high index enamel layer after firing step (c) of the present invention. The same defects were then again photographed after coating and firing for 10 minutes at 570 °C of a thin TiO_2 layer. Both defects are still slightly visible but the sharpness of their edges has completely disappeared. Healing of those surface defects took place.

Example

A 0.7 mm soda lime glass sheet was screen printed with a paste comprising 75 weight % of a high index glass frit (Bi_2O_3-B_2O_3-ZnO-Al_2O_3-SiO_2) and 25 weight % of an organic medium (ethyl cellulose and organic solvent) and submitted to a drying step (10 minutes at 150 °C).

The substrate was then fired for about 10 minutes at 570 °C resulting in a high index enamel layer having a thickness of 12 µm.

The resulting enamel-coated glass sheet was then coated by sol-gel deposition with a TiO_2 precursor and fired for about 10 minutes at 560 °C, resulting in a high index enamel layer incorporating a plurality of spherical voids near the surface.

The mean size of the spherical voids and the coverage rate (percentage of area of TiO_2 coated surface occupied by the spherical voids) were measured by image analysis. The below table shows the mean size of the spherical voids, the coverage rate and the haze ratio of the resulting substrate in comparison to an identical substrate submitted to the same treatment and analysis except for the TiO_2 coating step.

Table 1

	Negative control	Example
Thickness of the TiO_2 layer	0	22 nm

Mean size of spherical voids	-	1.8 µm
Coverage rate	-	77 %
IEL haze ratio	12.9 %	67.5 %

The high index enamel layer of the negative control was free of spherical voids located at the top of the enamel layer.

These experimental data clearly show that the spherical voids at the top of the enamel layer result from the interaction of the metal oxide layer with the overlying high index glass frit.

Fig 5 shows a top view (left) and cross-sectional view (right) of the sample corresponding to table 1.

REVENDICATIONS

1. A method for preparing a laminate substrate for a light emitting device, comprising at least the following steps :

(a) providing a glass substrate (1) having a refraction index, at 550 nm, of between 1.45 and 1.65,

(b) coating a glass frit (3) having a refractive index, at 550 nm, of at least 1.7 onto said glass substrate (1), said glass frit comprising at least 30 weight % of Bi_2O_3,

(c) firing the resulting frit coated glass substrate at a temperature above the Littleton temperature of the glass frit thereby forming a first high index enamel layer (4),

(d) coating a metal oxide layer (2) onto said first high index enamel layer, and

(e) firing the resulting coated glass substrate at a temperature above the Littleton temperature of the glass frit, comprised between 530 °C and 620 °C, thereby making react the metal oxide (2) with the underlying first high index enamel layer (4) and forming a second high index enamel layer (5) with a plurality of spherical voids (6) embedded in the upper section of the second high index enamel layer (5) near the interface with air.

2. The method according to claim 1, wherein the metal oxide layer has a thickness of between 5 and 60 nm, preferably of between 10 and 40 nm, more preferably of between 15 and 30 nm.

3. The method according to claim 1 or 2, wherein the metal oxide is selected from the group consisting of TiO_2, Al_2O_3, ZrO_2, Nb_2O_5, HfO_2,Ta_2O_5, WO_3, Ga_2O_3, In_2O_3 and SnO_2, and mixtures thereof.

4. The method according to any of the preceding claims, wherein the refractive index of the glass frit is comprised between 1.70 and 2.20, preferably between 1.80 and 2.10.

5. The method according to any of the preceding claims, wherein the glass frit comprises at least 50 weight %, preferably at least 60 weight % of Bi_2O_3.

6. The method according to any of the preceding claims, wherein the firing steps (c) and (e) are carried out at a temperature comprised between

540 °C and 600 °C.

7. The method according to any of the preceding claims, further comprising (f) coating a transparent electro-conductive layer (TCL) (8) on the second high index enamel layer (5).

8. A laminate substrate obtainable by the method of any of the preceding claims, comprising

(i) a glass substrate (1) having a refractive index of between 1.45 and 1.65,

(ii) a high index glass enamel layer (5) having a refractive index, at 550 nm, of at least 1.7, and comprising at least 30 weight % of Bi_2O_3,

characterized by the fact that a plurality of spherical voids (6) are embedded in the high index enamel layer (5) near the surface thereof, at least 95 %, preferably at least 99 %, and more preferably essentially all of the spherical voids having a diameter significantly smaller than the half-thickness of the high index enamel layer (5) and being located in the upper half of the high index enamel layer near the interface (7) with air.

9. The laminate substrate according to claim 8, wherein the spherical voids have an average equivalent spherical diameter of between 0.2 µm and 8 µm, preferably of between 0.4 µm and 4 µm, more preferably of between 0.5 µm and 3 µm

10. The laminate substrate according to claims 8 or 9, wherein the thickness of the second high index enamel layer (5) is comprised between 3 µm and 25 µm, preferably between 4 µm and 20 µm and more preferably between 5 µm and 15 µm.

11. The laminate substrate according to any of claims 8 to 10, further comprising (iii) a transparent electro-conductive layer (8) on the high index enamel layer (5).

12. The laminate substrate according to any of claims 8 to 11, wherein the spherical voids occupy at least 20 % of the surface and at most 80 % of the surface of the area previously covered by the metal oxide.

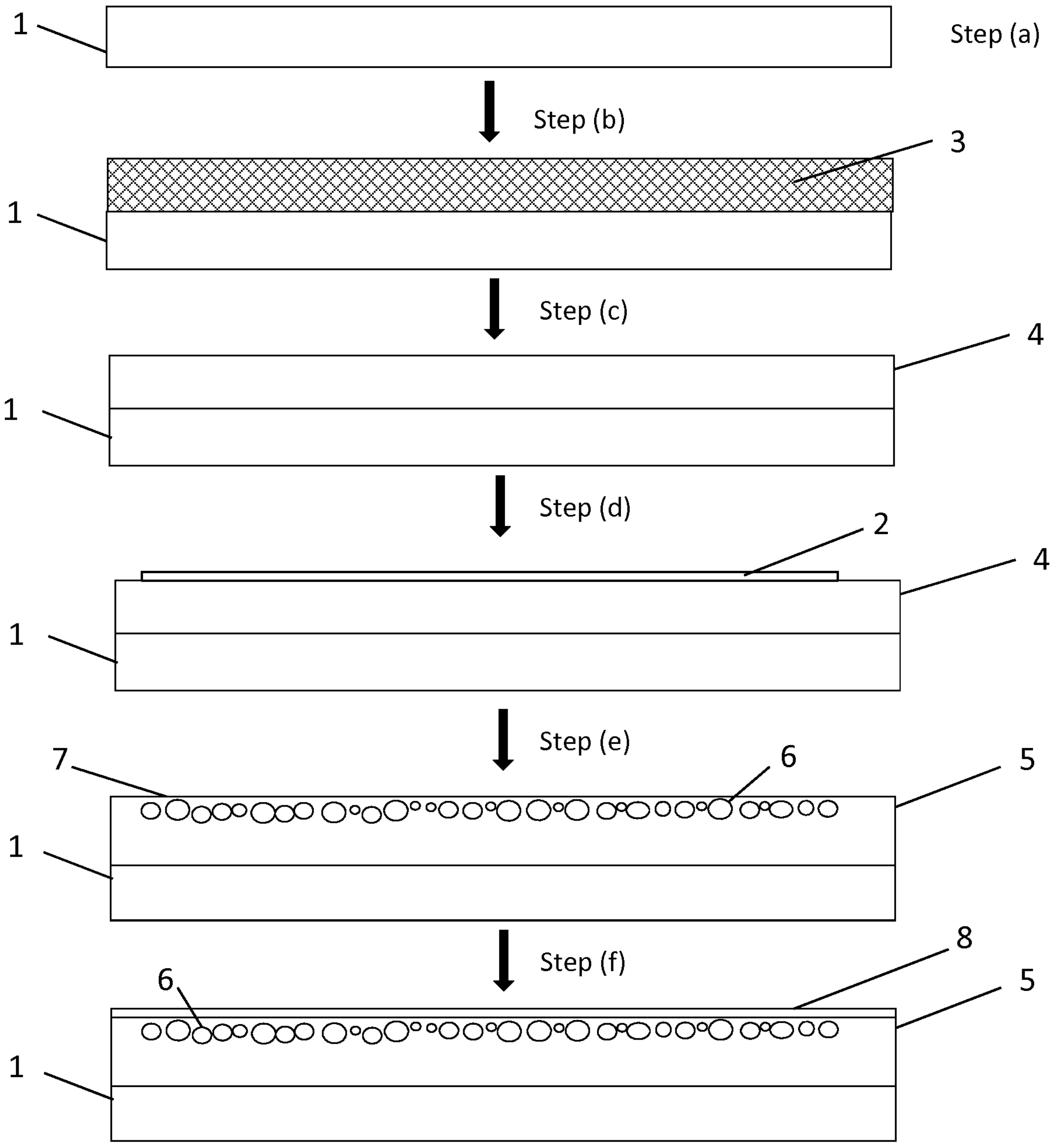


Figure 1

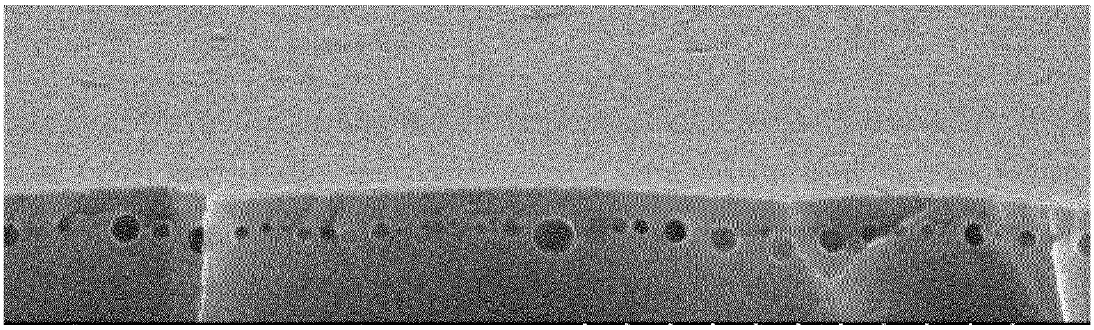


Figure 2

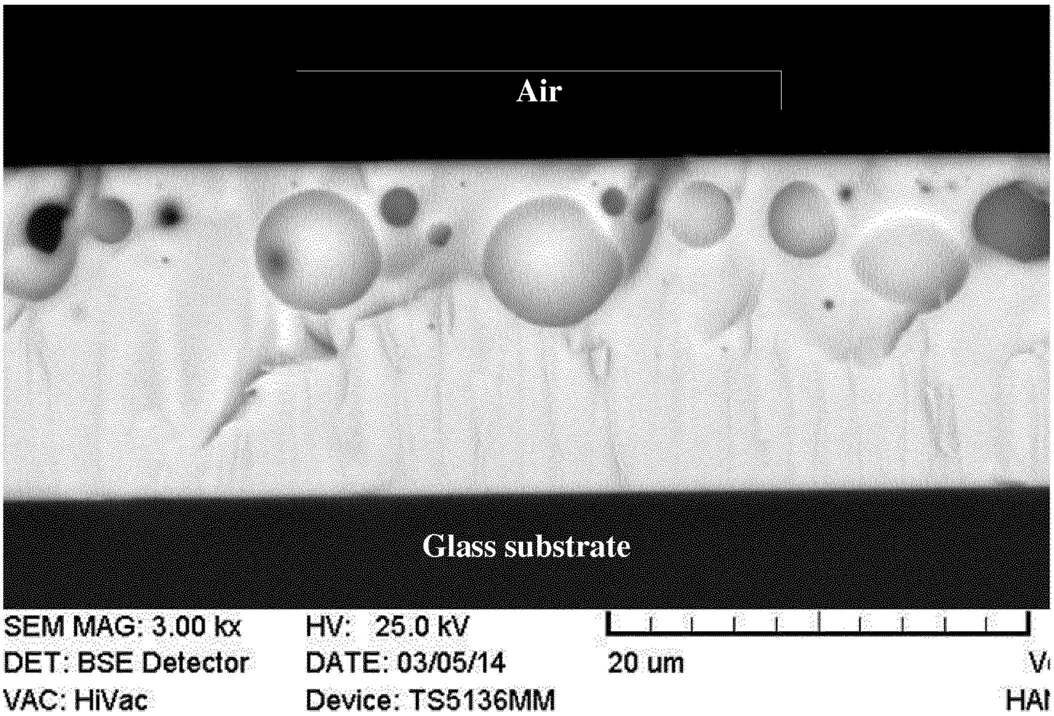


Figure 3

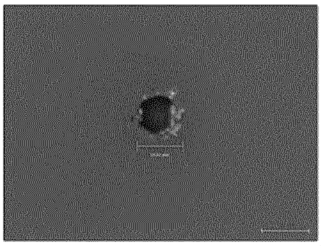
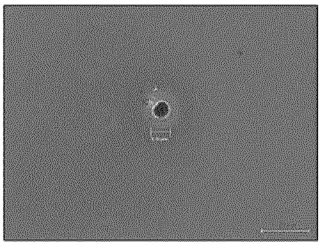
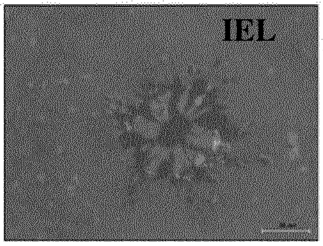
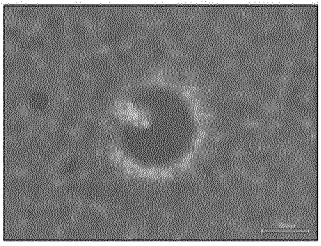
Steps	Defect 1	Defect 2
As TiO2 coated		
After annealing (@570C/ 10 min)	 	

Figure 4

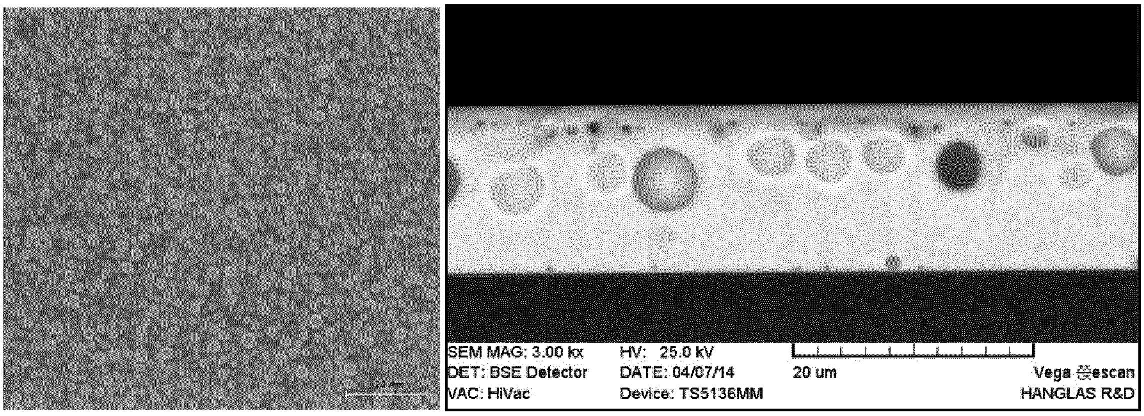


Figure 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/077393

A. CLASSIFICATION OF SUBJECT MATTER
INV. C03C17/00 C03C17/04 C03C17/34 C03C8/04 H01L51/00
H01L51/52 C03C21/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C03C H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/187735 A1 (SAINT GOBAIN [KR]) 19 December 2013 (2013-12-19) the whole document -----	1-12
A	EP 2 178 343 A1 (ASAHI GLASS CO LTD [JP]) 21 April 2010 (2010-04-21) the whole document -----	1-12
A	KR 101 436 548 B1 (SAMSUNG CORNING PREC MAT CO [KR]) 30 October 2014 (2014-10-30) the whole document -----	1-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
21 December 2015

Date of mailing of the international search report
07/01/2016

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Authorized officer
Heer, Stephan

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/077393

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