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(54) Title: BREAK RESISTANT AND SHOCK RESISTANT SAPPHIRE PLATE

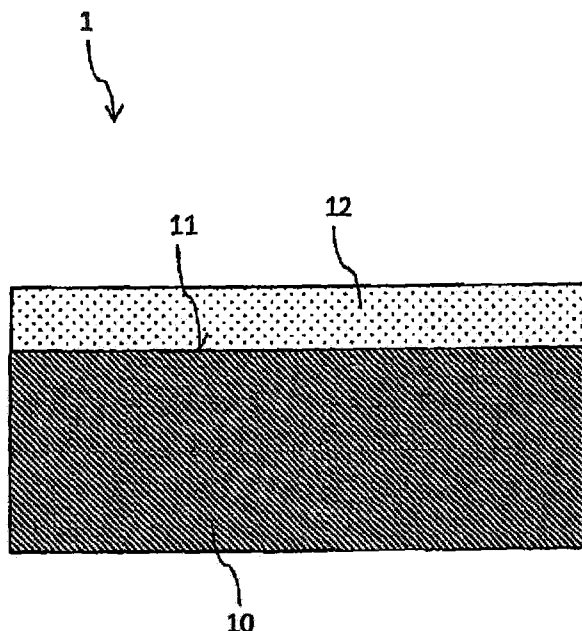


Fig. 1

(57) Abstract: The present invention relates to a break resistant sapphire plate and a corresponding production process, wherein the plate comprises a planar sapphire substrate (10) and at least one shock absorbing layer (12) arranged on a surface (11) of the substrate (10), and wherein the layer (12) has a thickness of between 0.1% to 10% of the thickness of the substrate (10).

Break resistant and shock resistant sapphire plate

Description

5 Technical field

The present invention relates to a break resistant and shock protected sapphire plate which is in particular intended to be used as a cover for display devices. Furthermore, the invention relates to a method for
10 producing said break resistant and shock protected sapphire plate.

Background

Mono-crystalline sapphire is characterized by an extraordinary hardness
15 and stretch resistance. Sapphire plates, generally also referred to as sapphire glass, are therefore frequently used in the watch industry. Insofar, it is desirable to broaden the scope of application of sapphire plates and to use them as transparent covers for display devices of electronic devices. It is generally conceivable to equip electronic
20 displays, for example of tablet computers, mobile phones and smartphones, with sapphire plates.

However, due to its crystalline, in particular mono-crystalline, structure, sapphire is relatively brittle. Relatively large and thin sapphire plates, as
25 they would have to be provided for example as covers for smartphones of tablet computers, therefore have a break resistance during bending and heavy impact, which is insufficient for practical application.

For production reasons, the surface of sapphire plates typically has
30 defects and/or micro-cracks. Such micro-cracks can propagate relatively fast in the plate material during bending or heavy impact and can ultimately lead to breaking of the sapphire plate.

In the publication of C.M. Liu, J.C. Chen, L.J. Hu, S.P. Lin "The effect of annealing, precipitation-strengthening, and compressive coating processes on sapphire strength", Material Science and Engineering A 420 (2006) 212-219, the hardening of sapphire by means of tempering is described, among others, during which the sapphire plates are heated up to temperatures of at least 1500° C for a relatively long time, i.e. approximately 24 hours.

Indeed, surface defects can thereby be removed. However, the method takes a relatively long time as well as being cost-intensive and energy-intensive. Furthermore, the coating of sapphire substrates with silicon nitride is described as an anti-reflection coating. Due to the subsequent thermal hardening process, to which the coating is subjected for at least an hour at a temperature of 1500° C, the applied silicon nitride layer can crystallize.

Since silicon nitride has a higher density in the crystalline state than in the amorphous state, a compressive stress can insofar be generated on the sapphire surface, due to which the micro-cracks or defects present on the surface bordering with the applied silicon nitride layer can virtually be pulled together and therefore be minimized. The sapphire plate can therefore be tensioned or pre-tensioned by the coating.

The refractive index of a silicon nitride layer is typically above 1.9. The refraction index of pure silicon nitride is even 1.98. In contrast, monocrystalline sapphire has an average refraction index of 1.74 in the range of the visible spectrum. Insofar, the silicon nitride layer alters the optical properties of a sapphire plate.

Consequently, silicon nitride is relatively highly reflective and has a reflectance on sapphire of over more than 30%, so that it can generally not be used for coating of cover plates of display devices.

By contrast, the present invention is based on the task to increase the impact resistance and breaking resistance of a sapphire substrate or a sapphire plate respectively, while influencing the optical properties of the sapphire plate, in particular with regard to optical transmission and reflection in the range of the visible spectrum, as little as possible. The invention is furthermore supposed to provide a preferably cheap, efficient and streamlined method for hardening of sapphire plates, which is in particular suitable for industrial mass production.

10 **Invention and advantageous effects**

This task is solved by a break resistant sapphire plate according to claim 1 as well as a method for its production according to claim 10.

15 The sapphire plate comprises a planar sapphire substrate and at least one shock absorbing layer arranged on one of the substrate surfaces. The shock absorbing layer has a thickness between 0.1% and 10% of the thickness of the substrate. Therefore, a comparatively thick layer is applied on the sapphire substrate which can provide a shock absorbing effect for the sapphire substrate underneath it.

The shock absorbing layer comprises a material or a material composition, which in comparison to the sapphire substrate underneath it is comparatively soft and plastically deformable. The shock absorbing layer applied to the substrate surface is in particular supposed to absorb mechanical stress applied on the layer, in particular selectively occurring hits or impacts by plastic deformation and if necessary conduct them within the layer away to the sides, so that a mechanical stress applied approximately perpendicular or at an angle on the sapphire plate is attenuated as much as possible, conducted to the sides or only applied to a lesser extent on the sapphire substrate underneath it.

Besides the layer thickness with regard to the thickness of the sapphire substrate, here, the substance or material composition of the layer as well its mechanical connection to the substrate is of importance.

5 It proves to be particularly advantageous if the layer extends over the entire substrate surface but is only bonded to the substrate surface at selected points. Insofar, the layer can lie at least sectionally comparatively loose on the substrate surface such that the mechanical stress applied to the shock absorbing layer is transferred within the
10 layer, but not transferred comparatively unattenuatedly from the layer into the bordering substrate due to a particularly firm and stiff connection of the layer and the substrate.

According to a further embodiment, the layer thickness is 0.5% to 5%,
15 0.8 to 3%, 1% to 2% or 1.2% to 1.5% of the thickness of the substrate. Embodiments with a layer thickness in the range of 1% to 2% of the substrate thickness prove to be particularly advantageous for the shock absorption. In particular, the impact and hit resistance of a sapphire plate could be noticeably raised during standardized experiments
20 comparable with the so-called ball drop test in accordance with UL-60950. During this test, a steel ball weighing 0.5 kg is dropped on the plate from a height of 1.3 m. Afterwards, the sapphire plates mechanically treated this way are subjected to a bending or breaking test.

25 This has shown that the sapphire substrate equipped with the shock absorbing layer has a significantly higher bending stiffness and breaking resistance in comparison to comparative but uncoated sapphire substrates even after the ball drop test.

30 According to a further embodiment, the sapphire substrate has a thickness of 200 μm to 2 mm, 300 μm to 1.5 mm, 500 μm to 1 mm or 600 μm to 800 μm . Also, embodiments can be provided which have a sapphire substrate thickness smaller than 1 mm, smaller than 800 μm ,

smaller than 600 μm or smaller than 400 μm . At a typical thickness of the sapphire substrate of approximately 0.4 mm, the thickness of the layer applied to the substrate can in particular be 4 μm and higher.

- 5 Insofar, according to a further embodiment, it is provided that the layer thickness independent of the sapphire substrate thickness is at least 1 μm , at least 2 μm , at least 3 μm , at least 4 μm or at least 5 μm .

10 The layer thickness can typically be chosen with regard to the substrate thickness. Furthermore, the optical properties of the shock absorbing layer are to be considered. Ideally, the shock absorbing layer has similar, almost identical optical properties as the planar sapphire substrate underneath it. Therefore, the optical properties of a sapphire plate produced this way, even after application of a comparatively thick layer
15 on the planar sapphire substrate, can be almost unchanged in comparison to the sapphire substrate.

20 According to a further embodiment, the connection between the sapphire substrate and the shock absorbing layer perpendicular to the level of the sapphire substrate has a smaller tensile strength than the sapphire substrate and/or the layer itself. It is here in particular provided that the adhesion between the substrate surface and the layer is to be comparatively badly formed such that with regard to a microscopic scale, the layer is only sectionally connected with the substrate surface.

25 Such a comparatively loose arrangement of the layer and the substrate surface is on the one hand advantageous for the shock absorption of the applied layer and on the other hand for conducting mechanical impacts within the layer. Due to the comparatively bad adhesion between the
30 shock absorbing layer and the sapphire substrate, a local elastic or plastic deformation of the layer is not immediately transmitted into the sapphire substrate beneath it. The quality of the adhesion of the layer on the substrate surface is as far as possible to be chosen according to the respective provided coating process such that the layer in its entirety is

removable from the sapphire substrate due to a force directly in the direction of the surface normal and applied inversely on the sapphire substrate and the layer.

- 5 The surface compound between the substrate surface and the layer applied on the substrate is therefore to be formed more weakly than the tensile strength of the layer as well as the tensile strength of the sapphire substrate itself.
- 10 The layer here has at least 50 wt.-% of aluminum oxide (Al_2O_3). Since sapphire substantially contains crystalline aluminum oxide, applying a layer having a high amount of aluminum oxide to a sapphire substrate alters its optical properties at the most marginally.
- 15 It initially seems to be counter-intuitive to apply an aluminum oxide layer to a sapphire substrate. However, experiments have shown, that by coating the sapphire substrate with a layer having at least 50 wt.-% of aluminum oxide, the break resistance, the hit resistance as well as the bending strength of the sapphire substrate, thus of the sapphire
- 20 substrate and the sapphire plate with the at least one layer can be increased significantly in comparison to the uncoated sapphire substrate.

- 25 Due to the high amount of aluminum oxide in the layer applied to the sapphire substrate, the optical properties of the sapphire substrate are altered, if at all, only negligibly.

- 30 According to a further embodiment, the layer comprises amorphous aluminum oxide. This has a higher thermal expansion coefficient in comparison to a crystalline aluminum oxide, i.e. in comparison to sapphire. Since the coating process is done at significantly elevated temperatures compared to room temperature, approximately in the range from 300° C to 500° C, in particular in the range of approximately 400° C, the applied layer contracts during cooling of the coated sapphire

plate significantly more than the sapphire substrate. Insofar, can the layer apply compressive stress on the substrate.

5 According to a further embodiment, the layer applied to the sapphire substrate substantially comprises aluminum oxide. It can also substantially consist of aluminum oxide. It is, however, also conceivable and in particular due to the respective coating process, that the layer applied to the sapphire substrate also comprises other components or materials.

10

It is insofar conceivable that the layer comprises at least 60 wt.-% of aluminum oxide, at least 70 wt.-% of aluminum oxide, at least 80 wt.-% of aluminum oxide or even more than 90 wt.-% of aluminum oxide.

15

According to a further embodiment, besides aluminum oxide, the layer comprises carbon, hydrogen and/or nitrogen. In particular, the layer can comprise 0 to 5 wt.-% carbon, 0 to 10 wt.-% of hydrogen and/or 0 to 5 wt.-% of nitrogen. These additional materials in the layer are intrinsically included in the layer due to the coating processes.

20

If, for example, a plasma-assisted chemical steam separator method, a so-called plasma-CVD process, is used to apply the layer, an aluminum oxide deposition on the sapphire substrate can occur especially efficiently with comparatively high deposition rates by supplying trimethylaluminum (TMA) and nitrous oxide. The plasma generation which takes place in a plasma reactor at a predetermined temperature and a predetermined pressure and the corresponding chemical reaction can inevitably lead to the inclusion of carbon, hydrogen and/or nitrogen parts in the applied layer.

25

30 According to a further embodiment, the layer applied to the sapphire substrate is substantially transparent for electromagnetic radiation in the visible wavelength range. Substantially transparent here means a transmittance of at least 80%, 85% or of at least 90%.

In a further aspect, the invention further relates to a method for producing a break-resistant sapphire plate. In a first method step, a planar sapphire substrate is provided which, in a subsequent step, is provided, in particular coated, with a shock-absorbing layer. At least one surface of the substrate is thereby coated with a break-resistant layer, wherein the layer has a layer thickness between 0.1% - 10% of the thickness of the substrate.

This results in the previously described advantages with regard to the breaking resistance and bending flexibility of the sapphire plate, which was shock-protected by means of the applied layer.

Optionally, the provided planar sapphire substrate can be subjected to a thermal pretreatment prior to the coating process, such as tempering or annealing. Thereby, any micro cracks of the substrate per se present on the substrate surface can at least be closed sectionally, but at least be minimized.

According to a further embodiment, the layer is applied to the substrate with the assistance of plasma. For this purpose, the substrate is inserted into a plasma treatment chamber, in which a plasma is ignited at a predetermined pressure and a predetermined temperature by introducing at least one or more process gases and by providing energy. Reaction products of the reaction gases inserted into the plasma treatment chamber can hereby deposit on the surface of the substrate and can therefore form the surface-tensioned layer on the substrate.

According to a further embodiment, the layer can also be applied to the surface of the substrate by way of a sputtering process. A sputtering target is hereby subjected to ion bombardment, whereby target ions are ejected from the target and are finally deposited on the surface of the substrate. Here, it is in particular provided to use a ceramic aluminum oxide target or an aluminum target. When using an aluminum target,

oxygen or gases containing oxygen respectively are in particular to be provided in the corresponding reaction chamber to facilitate the formation of aluminum oxide and its deposition on the substrate surface.

5 According to a further embodiment, the layer is applied to the substrate by way of a plasma-assisted CVD process. Hereby, in particular a PECVD method (Plasma-Enhanced-Chemical-Vapor-Deposition) is used.

10 For the plasma-assisted CVD process according to a further embodiment, in particular trimethylaluminum (TMA) and nitrous oxide are used as reaction gases. The reaction gases trimethylaluminum (TMA) and nitrous oxide are used here in a ratio of at the most 1/2, 1/4, 1/8, 1/16, 1/24 or 1/32. This means that for one part of TMA, there are
15 at least 32 parts of nitrous oxide. The ratio mentioned here specifies the ratio of the amounts of substance inserted into a plasma reactor per unit of time.

Extensive experiments with varying reaction gas ratios have shown that
20 using a trimethylaluminum to nitrous oxide ratio of approximately 1/16 in a plasma CVD process generates excellent surface-tensioned layers on the sapphire substrate which increase the breaking resistance and bending flexibility of the entire sapphire plate in comparison to the uncoated sapphire substrates and in comparison to the coated sapphire
25 substrates, which were generated using a different reaction gas ratio.

Using a reaction gas mixture of 16 nitrous oxide parts for each trimethylaluminum part also proves to be especially advantageous for the scratch resistance of the applied layer. The scratch resistance of a
30 layer generated with a process gas mixture ratio of 1/16 is visibly better than the scratch resistance of layers which were generated with a process gas mixture ratio of for example 1/8 or 1/32.

Short description of the figures

In the following description of an embodiment, additional features of the invention will be explained with reference to the drawing. Fig. 1 shows a schematic cross section of a surface-tensioned sapphire plate.

5

The sapphire plate shown in Fig. 1 comprises a planar sapphire substrate 10 whose planar surface 11 is provided with a shock-absorbing layer 12. The layer 12 applied to the sapphire substrate 10 can generally comprise different, shock-absorbing materials and substances.

10

According to a particular embodiment, the layer comprises at least 50 wt.-% of aluminum oxide.

The thickness of the sapphire substrate 10 can be 200µm to 2mm, 300µm to 1.5 mm, 500µm to 1mm or 600 µm to 800mm. Also, embodiments can be provided which have a thickness of the sapphire substrate 10 smaller than 1mm, smaller than 800µm, smaller than 600µm or smaller than 400µm. At a typical thickness of the sapphire substrate 10 of approximately 0.4 mm, can the thickness of the layer 12 applied to the substrate be in particular 4µm and more.

20

Due to a comparatively thick coating 12, in particular of 0.5% to 1.5% or of 0.8% to 1.2% of the substrate thickness, can a particularly high shock-absorbing effect be provided by layer 12. The layer thickness can be approximately 4µm for a substrate 10 of approximately 400µm thickness. The layer can however also have a layer thickness of at least 1µm, at least 1.5µm, at least 2µm, at least 3µm, at least 4µm or of at least 5µm independently of the thickness of the sapphire substrate 10.

25

Sapphire substrate 10 can typically be oriented in parallel with its crystallographic A or C axis to the surface normal of the planar surface 11. Insofar, either the crystalline A level or the C level of the mono-crystalline sapphire substrate 10 can run along the coated

30

substrate surface 11 and it can insofar coincide with the border layer between substrate surface 11 and coating 12.

- 5 Layer 12 comprising a comparatively high amount of aluminum oxide can be applied to the substrate by way of sputtering or by way of a plasma-assisted steam deposition process at a comparatively high temperature, for example at temperatures between 350° C and 450° C, in particular at temperatures of, for example, approximately 400° C.

Claims

1. Break resistant sapphire plate comprising a planar sapphire substrate (10) and at least one shock absorbing layer (12) arranged on the surface (11) of the substrate (10), wherein the layer (12) has a layer thickness of 0.1% to 10% of the thickness of the substrate (10) and wherein the layer (12) is only bonded to the surface (11) of the substrate (10) at selected points.
2. Sapphire plate according to claim 1, wherein the layer thickness is 0.5% to 5%, 0.8% to 3%, 1% to 2%, or 1.2% to 1.5% of the thickness of the substrate (10).
3. Sapphire plate according to any one of the preceding claims, wherein the thickness of the sapphire substrate (10) is 200 μm to 2 mm, 300 μm to 1.5 mm, 500 μm to 1 mm or 600 μm to 800 μm .
4. Sapphire plate according to any one of the preceding claims, wherein the layer thickness is at least 1 μm , at least 1.5 μm , at least 2 μm , at least 3 μm , at least 4 μm or at least 5 μm .
5. Sapphire plate according to any one of the preceding claims, wherein the connection between the sapphire substrate (10) and the shock absorbing layer (12) has a weaker tensile strength perpendicular to the level of the sapphire substrate (10) than the sapphire substrate (10) and/or the layer (12).
6. Sapphire plate according to any one of the preceding claims, wherein the layer (12) has at least 50 wt.-% of amorphous Al_2O_3 .
7. Sapphire plate according to any one of the preceding claims, wherein the coated surface (11) of the sapphire substrate (10) coincides with the crystalline A level of sapphire.

8. Sapphire plate according to any one of the preceding claims, wherein the layer (12) comprises at least 50 wt.-% of Al_2O_3 , at least 60 wt.-% of Al_2O_3 , at least 70 wt.-% of Al_2O_3 , at least 80 wt.-% of Al_2O_3 or even more than 90 wt.-% of Al_2O_3 .
9. Sapphire plate according to one of claims 1 to 7, wherein the layer (12) comprises up to 5 wt.-% of carbon, up to 10 wt.-% of hydrogen and/or up to 5 wt.-% of nitrogen.
10. Method for producing a sapphire plate according to any one of the preceding claims, comprising the steps of:
 - providing a planar sapphire substrate (10),
 - coating at least one surface (11) of the substrate (10) with a shock absorbing layer (12) having a layer thickness between 0.1% to 10% of the thickness of the substrate (10).
11. Method according to claim 10, wherein the layer (12) is applied to the substrate (10) with the assistance of plasma.
12. Method according to claim 10 or 11, wherein the layer (12) is applied to the surface (11) of the substrate (10) by means of a sputtering process.
13. Method according to one of claims 10 or 11, wherein the layer (12) is applied to the substrate (10) by means of a plasma-assisted CVD process and wherein the reaction gases for the plasma CVD process trimethylaluminum (TMA) and nitrous oxide are used in a mole ratio of at most 1/2, 1/4; 1/8; 1/16; 1/24 or 1/32.

AMENDED CLAIMS

received by the International Bureau on 17 July 2014 (17.07.2014)

1. Break resistant sapphire plate comprising:
 - a planar sapphire substrate (10);
 - at least one shock absorbing layer (12) arranged on the surface (11) of the substrate (10),
 - wherein the layer (12) has a layer thickness of 0.1% to 10% of the thickness of the substrate (10); and
 - a connection positioned between the sapphire substrate (10) and the shock absorbing layer (12), perpendicular to the axis of the sapphire substrate (10),
 - wherein the connection has a smaller tensile strength than at least one of the sapphire substrate, and the shock absorbing layer.
2. Sapphire plate according to claim 1, wherein the layer thickness is 0.5% to 5%, 0.8% to 3%, 1% to 2%, or 1.2% to 1.5% of the thickness of the substrate (10).
3. Sapphire plate according to any one of the preceding claims, wherein the thickness of the sapphire substrate (10) is 200 μm to 2 mm, 300 μm to 1.5 mm, 500 μm to 1 mm or 600 μm to 800 μm .
4. Sapphire plate according to any one of the preceding claims, wherein the layer thickness is at least 1 μm , at least 1.5 μm , at least 2 μm , at least 3 μm , at least 4 μm or at least 5 μm .
5. Sapphire plate according to any one of the preceding claims, wherein the connection between the sapphire substrate (10) and the shock absorbing layer (12) has a weaker tensile strength perpendicular to the level of the sapphire substrate (10) than the sapphire substrate (10) and/or the layer (12).

6. Sapphire plate according to any one of the preceding claims, wherein the layer (12) has at least 50 wt.-% of amorphous Al_2O_3 .
7. Sapphire plate according to any one of the preceding claims, wherein the coated surface (11) of the sapphire substrate (10) coincides with the crystalline A level of sapphire.
8. Sapphire plate according to any one of the preceding claims, wherein the layer (12) comprises at least 50 wt.-% of Al_2O_3 , at least 60 wt.-% of Al_2O_3 , at least 70 wt.-% of Al_2O_3 , at least 80 wt.-% of Al_2O_3 or even more than 90 wt.-% of Al_2O_3 .
9. Sapphire plate according to one of claims 1 to 7, wherein the layer (12) comprises up to 5 wt.-% of carbon, up to 10 wt.-% of hydrogen and/or up to 5 wt.-% of nitrogen.
10. Method for producing a sapphire plate according to any one of the preceding claims, comprising the steps of:
 - providing a planar sapphire substrate (10),
 - coating at least one surface (11) of the substrate (10) with a shock absorbing layer (12) having a layer thickness between 0.1% to 10% of the thickness of the substrate (10).
11. Method according to claim 10, wherein the layer (12) is applied to the substrate (10) with the assistance of plasma.
12. Method according to claim 10 or 11, wherein the layer (12) is applied to the surface (11) of the substrate (10) by means of a sputtering process.
13. Method according to one of claims 10 or 11, wherein the layer (12) is applied to the substrate (10) by means of a plasma-assisted CVD process and wherein the reaction gases for the plasma CVD

process trimethylaluminum (TMA) and nitrous oxide are used in a mole ratio of at most $1/2$, $1/4$; $1/8$; $1/16$; $1/24$ or $1/32$.

Statement under Art. 19(1) PCT

Claim 1 is amended based on the observations outlined in the Written Opinion of the ISA. In particular, the amendment aims to overcome the novelty objections raised in the Written Opinion by clarifying the connection between the sapphire substrate and the shock absorbing layer. This connection has a weak tensile strength, which reduces the propagation of shock from the shock absorbing layer into the sapphire substrate. Such a connection is not disclosed in the cited prior art. This amendment furthermore aims to overcome the objections with regard to inventive step since the cited prior art does not render a shock absorbing layer and its connection to the substrate according to amended claim 1 obvious. The cited prior art discloses bonding brittle sapphire parts to a carrier such as plastic or titanium. It does not disclose or hint at a shock absorbing layer connected to a sapphire substrate as described by the amendments made claim 1. This amendment thus renders claim 1 inventive over the cited prior art.

1/1

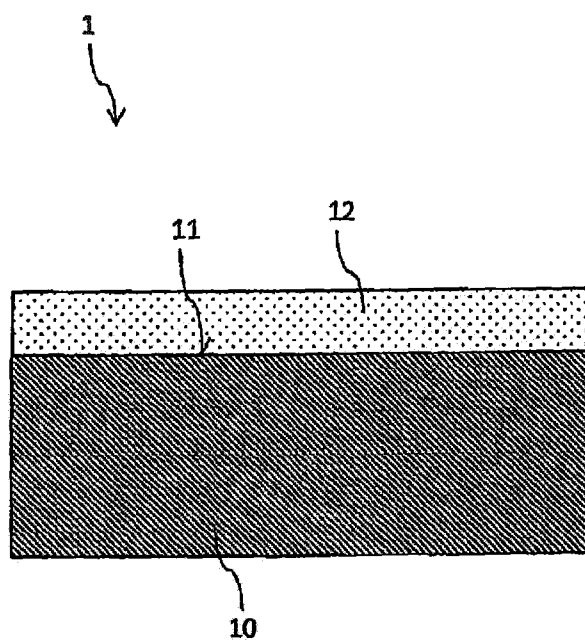


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/054819

A. CLASSIFICATION OF SUBJECT MATTER

INV. C30B29/20 C23C14/08 C23C16/40
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)

C23C C30B

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, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	P H KOBRIN ET AL: "Compressive thin films for increased fracture toughness", PROCEEDINGS OF SPIE, vol. 683, 1 January 1986 (1986-01-01), - 19 August 1986 (1986-08-19), pages 139-143, XP55114398, US	1,3,4,6, 8-10,12
Y	ISSN: 0277-786X, DOI: 10.1117/12.936429 page 140 - page 142; figure 1; table 1	2,5,7, 11,13
Y	----- US 2004/102229 A1 (HUTCHISON MARK [GB]) 27 May 2004 (2004-05-27) paragraph [0062] ----- -/-	2,5,7, 11,13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

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Date of mailing of the international search report

30/04/2014

Name and mailing address of the ISA/

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Cook, Steven

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/054819

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 102 400 213 A (ANHUI KANGLAN PHOTOELECTRIC CO LTD) 4 April 2012 (2012-04-04) claims 1,2 -----	1-13
A	US 3 809 574 A (DUFFY M ET AL) 7 May 1974 (1974-05-07) the whole document -----	10-13
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