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(71) Applicant *(for all designated States except US)*: **BENEQ OY** [FI/FI]; Ensimmäinen Savu, P.O. Box 262, FI-01510 Vantaa (FI).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **RAJALA, Markku** [FI/FI]; Jousitie 3, FI-01280 Vantaa (FI). **SEPPÄLÄINEN, Erkki** [FI/FI]; Martinlaaksontie 40 C 16, FI-01620 Vantaa (FI).

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(54) Title: COATING PROCESS, APPARATUS AND USE

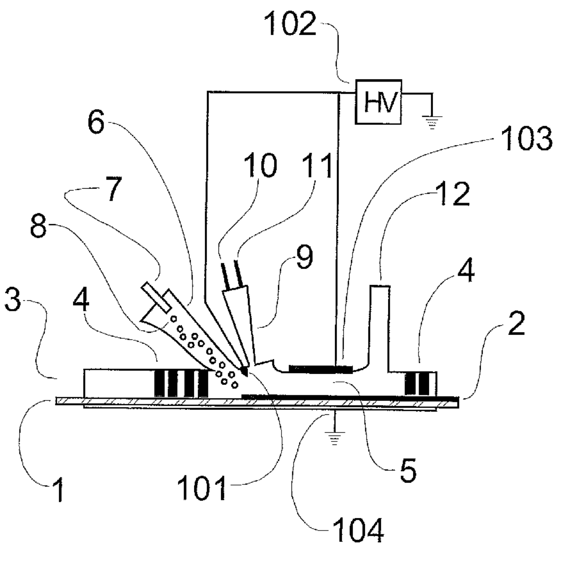

Fig. 1

(57) Abstract: Aerosol-assisted process for depositing a coating (2) on a substrate (1). The process comprises first precursor flow comprising aerosol and second precursor flow comprising at least one reactant. The first flow comprises droplets and is essentially free of reactant required for coating (2) formation. An apparatus for carrying out the process, and use of such an apparatus is also disclosed.

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COATING PROCESS, APPARATUS AND USE

Field of invention

The invention relates to an aerosol-assisted coating deposition process, especially to a pyrolytic aerosol assisted coating processes where the precursors are allowed to react on the substrate surface or at the vicinity of the substrate surface. In the invented process the aerosol flow in the first conduit is kept free from at least one reactant required for the coating formation. Said reactant and its flow is fed to the deposition chamber as a second precursor flow, for example from a second conduit.

Description of the state of the art

As such, spray coating is a known method for applying a coating. Typical examples of spray-coating are, for example, spray painting and pigment coating of paper.

Patent publication US 4,656,963, 14 April 1987, Takashi Yonehara et al., discloses a method for forming an extremely thin film on the surface of an object. In the method, aerosol is produced from the precursor material and introduced onto the surface of the substrate to be coated, and after evaporation of the solvent, a thin film is formed on the surface. The publication discloses the production of aerosol particles by ultrasonics, ranging in size from 1.5 to 10 micrometres. The publication provides no description of how the aerosol particles are introduced onto the surface of the substrate.

Patent publication US 4,728,353, Glaverbel, 1 March 1988, discloses an apparatus for forming a pyrolytic metal compound coating on a hot glass substrate. For the operation of the apparatus, it is essential that the gas atmosphere in the immediate vicinity of the face of the glass substrate is controlled by means of supplying preheated gas thereto that forms a protective atmosphere in the vicinity of the face of the glass substrate. The protective atmosphere makes it possible to prevent the entry of ambient air into the coating area. The publication discloses that the preheated gas is preheated air, meaning that the coating reactions take place in an oxygen-rich atmosphere. The feeding of coating precursor material by means of spraying is disclosed in the publication, but the diameter of the mist droplet is not disclosed.

Patent publication US 5,540,959, Xingwu Wang, 30 June 1996, discloses a method for preparing a coated substrate using mist particles. In the method, small droplets are produced that are heated with radio frequency energy to vaporise the droplets, after which the vapour is deposited onto a substrate.

The prior art does not disclose the advantages of having the fluid dispersed into small droplets and keeping the droplets away from a reactive precursor before the droplets are in close contact with the substrate surface.

Summary of the invention

The invention solves the problems of the prior art by an aerosol-assisted coating deposition process where the reaction of the precursor at too early stage is avoided. In this context, such an unwanted, premature reaction can happen in a too early stage in a temporal or in a spatial sense. The aerosol-assisted coating deposition process is preferably a pyrolytic coating deposition process, such as an aerosol-assisted chemical vapor deposition (AACVD) process or a spray pyrolysis processes, but other deposition processes where aerosols are applied are within the scope of this invention. An aerosol is a mixture of at least one gas component and particles, in this case especially liquid particles, or droplets. The premature reaction of the coating precursor is avoided by feeding at least one precursor, i.e. first precursor flow, in aerosol form and keeping this aerosol flow essentially free from reactant-containing compounds, e.g. free from oxygen or sulfur, which may be either in gaseous or liquid form. Terms “aerosol flow" and "first precursor flow" are used interchangeably in this application. It is also to be noted that even though "first precursor flow" is a singular word, it can contain one or many different precursor chemicals. At the coating formation zone of the process said at least one precursor is allowed to react with the reactant-containing compound, i.e. second precursor flow, and a coating is formed. In this application, terms "second precursor flow" and "reactant flow" are used interchangeably. It is also to be noted that even though "second precursor flow" is a singular word, it can contain one or many different precursor or reactant chemicals.

The droplets are evaporated at or near a substrate which may be e.g. glass, ceramic or metal substrate. Typical substrates include thin silicon substrate and flat glass substrate. Especially in the case of manufacturing transparent conductive oxide (TCO) coatings on glass the substrate is a flat glass substrate, typically having a thickness of 1 to 6 mm. The substrate may form an essentially continuous ribbon or the substrate may consist of separate pieces or wafers.

When manufacturing chemical vapor deposited coatings, such as TCO coatings, the droplets are preferably evaporated before hitting the surface. When manufacturing coatings which are based on the decomposition of a precursor, such as cadmium sulfide (CdS) coatings, it is preferred to allow the droplets to hit the surface. The present invention is valid in both coating processes.

In some embodiments of the invention the coating process may require several precursors which are not miscible with each other. An example of such precursor system is the production of fluorine doped tin oxide (FTO) coating from an organic compound of tin, such as monobutyltin trichloride (MBTC) and a tin-doping fluorine source, such as hydrogen fluorine (HF) or an organic source, such as trifluoroacetic acid (TFA, $C_2HF_3O_2$). MBTC and TFA cannot be mixed together without an additional solvent, which usually comprises oxygen, such as methyl alcohol (CH_3OH). However, the process described in the present invention allows atomizing MBTC and TFA from different atomizing nozzles, evaporating both precursors and then allowing them to react with an oxygen-containing precursor. The small amount of oxygen in the TFA does not affect the coating process adversely. An analogue process applies for other tin doping materials, such as antimony (Sb).

One advantage of a droplet-based deposition process, such as the AACVD or spray pyrolysis process compared to a traditional CVD process is that the droplets can be charged and then electrical forces, such as an electrical field, may be used to exert forces on the droplets for optimal guidance, directioning and deposition of the droplets. Droplet charging may be realized in various ways, such as by diffusion charging or by field charging, both methods familiar for a person skilled in the art. The droplets are charged essentially in similar way independent on their composition. When the atomized droplets have a diameter of less than 10 micrometers they may be charged to carry an absolute charge equivalent to some tens of elementary charges and their mobility in an electric field is reasonably high so that the charged droplets can be effectively guided.

The reactant-containing compound may be fed into the coating formation zone either as gases or as an aerosol. In one embodiment of the invention the reactant-containing compound is preferably water (H_2O), as water radically increases the coating growth rate of FTO coatings. When the FTO coating is formed on glass substrates at relatively low temperatures (below 650°C), it is preferred to supply water in vapor form, because evaporating the water droplets is energy-consuming and would thus cool down the surface of the glass substrate, which is unfavorable to the coating growth. For optimal growth of a

FTO coating it is found to be helpful to supply part of the reactant-containing compound as gaseous oxygen.

Brief description of the drawings

In the following, the invention will be described in more detail with reference to the appended principle drawing, in which

Fig. 1 shows the principle drawing of the invented process and apparatus;

Fig. 2 shows an embodiment of the invented apparatus, where the atomized aerosol is guided by additional gas flows;

Fig. 3 shows an embodiment for the atomizing nozzle; and

Fig. 4 shows an embodiment with two atomizing nozzles for different liquid precursors.

For the sake of clarity, the figures only show the details necessary for understanding the invention. The structures and details which are not necessary for understanding the invention and which are obvious for a person skilled in the art have been omitted from the figures in order to emphasize the characteristics of the invention.

Detailed description of preferred embodiments

Figure 1 shows a principle drawing of the process and apparatus 3 for depositing coating 2 on substrate 1. Apparatus 3 includes first conduit 6 for a liquid precursor which is atomized to droplets 8 by an atomizer 7. The mean diameter of droplet 8 is preferably low enough so that the gravitational forces affecting the droplet settling are low. Thus the droplet 8 diameter is preferably less than 10 micrometers and more preferably less than 3 micrometers. The droplets 8 and the gas used for atomizing the droplets essentially do not contain a reactant which is required to turn the precursor in the droplet to the material of coating 2. For example in the case of forming a tin oxide (SnO_2) coating from monobutyltin trichloride (MBTC, $C_4H_9SnCl_3$), the gas flow does not comprise oxygen in the form of e.g. gaseous oxygen (O_2) or water vapor (H_2O). The word ‘essentially’ is used in here to clarify that small amounts of oxygen can be included e.g. in doping materials as long as their amount is so low that they do not adversely create unwanted gas-phase reactions. For example when doping tin oxide with fluorine, the droplets 8 may include small amounts of trifluoroacetic acid, $C_2HF_3O_2$.

First conduit 6 leads into deposition chamber 5 where the growth of coating 2 takes place. The coating 2 growth requires a second precursor flow, also defined as a reactant flow from the second conduit 9. Such flow can be for example the flow of an oxygen-containing precursor when forming the tin oxide coating from MBTC. The second conduit 9 includes at least one precursor supply channel 10, but may include other supplies 11 as well. For example in the formation of SnO_2 coatings channel 10 is used to supply water vapor and channel 11 is used to supply gaseous oxygen or air and the vapor and gas flows are mixed in the second conduit 9 before feeding into the deposition chamber 5.

In one embodiment the invented process and apparatus are used to form a coating 2 by chemical vapor deposition. In such embodiment it is preferred to heat the substrate to an elevated temperature, typically above 500°C, which allows thermal CVD coating growth of e.g. SnO_2 coatings. In the CVD process it is preferable to create high precursor vapor pressures on the surface of substrate1. In one embodiment of the invention droplets 8 are charged by a charger 101 and an electric field created between electrode 103 and co-electrode 104 is used to guide droplets 8 close to the surface of substrate 1. In a preferred embodiment, the charger 101 is a corona charger and the required high voltage is supplied from a high voltage generator 102.

The second precursor flow from second conduit 9 may comprise other precursors required for the coating formation. For example in the case of forming fluorine doped tin oxide coatings the precursor flow from second conduit 9 may comprise fluorine precursor flow.

Figure 3 shows the preferred atomizer 7 used to realize the present invention. Liquid comprising a precursor is fed into the atomizer from channel 14 and the atomizing gas from channel 15. A pressure chamber 16 is used to provide uniform gas flow through channel 17. On the tip 18 of the liquid feed tube 14 the gas flow atomizes the liquid into primary droplets. Chokes 19 homogenize the droplets and fine droplets 8 with narrow droplet size distribution exit from the atomizer 7. The atomizer gas fed through channel 15 may also contain a gaseous precursor or a dopant such as a gaseous fluorine source used in the production of fluorine-doped tin oxide coatings.

In many cases it is beneficial to be able to use precursors which are immiscible. Figure 2 shows an embodiment for such precursors where two different atomizers 7 (first atomizer) and 7* (second atomizer) or set of two different atomizers 7 and 7* (first and second atomizers, respectively) are coupled into first conduit 6 and different precursor are atomized in atomizer 7 and atomizer 7* or in a set of two different atomizers 7 and 7* to droplets 8 and 8*. Additional gas flows 13 are used to guide droplets 8 and 8* so that they move sideways in first conduit 6 and a homogeneous mixture of droplets 8 and 8* is achieved before the droplets 8 and 8* evaporate on or at the vicinity of substrate 1. In other words, gas flows 13 widen the aerosol flow pattern. Gas flow 13 may include a precursor or a dopant such as a gaseous fluorine source for the production of fluorine doped tin oxide.

The atomizers may also be arranged towards each other as shown in Figure 4. When atomizers 7 and 7* are directed essentially towards each other, the droplets 8 and 8* are effectively mixed. The atomizing gases 14 may differ from each other in different atomizers.

The inventors have referred to the formation of doped or undoped SnO_2 coating in the text above. However, the invention is not limited to the formation of this particular coating, but the invented process and apparatus can be used e.g. in the formation of SiO_xN_y, SiO_xC_y, CdS, GaAs, In_2O_3:Sn (ITO), SnO_2:Sb (ATO), ZnO:Al (AZO), TiO_2, doped TiO_2 and various other coatings.It is possible to produce various embodiments of the invention in accordance with the spirit of the invention. Therefore, the above-presented examples must not be interpreted as restrictive to the invention, but the embodiments of the invention can be freely varied within the scope of the inventive features presented in the claims.

Claims

1. An aerosol-assisted process for depositing a coating (2) on a substrate (1), comprising first precursor flow and second precursor flow, the first precursor flow comprising droplets (8) and being essentially free of at least one reactant present in the second precursor flow, wherein the first precursor flow comprises droplets of at least two different compositions (8, 8*).
2. The process of claim 1, wherein the droplets (8, 8*) essentially vaporize before reaching the substrate (1).
3. The process as in any of the previous claims wherein the mean droplet (8, 8*) diameter is less than 10 micrometers.
4. The process as in any of the previous claims, wherein the first precursor flow comprises droplets (8, 8*) with precursor for tin oxide (SnO_2) deposition.
5. The process of claim 4, wherein the precursor for tin oxide deposition is an organic compound of tin.
6. The process as in any of the previous claims, wherein the first precursor flow comprises droplets (8, 8*) with precursor for doping tin oxide (SnO_2).
7. The process of claim 6, wherein the precursor for tin oxide doping is an organic compound of fluorine.
8. The process as in any of the claims 4-7, wherein the second precursor flow comprises water (H_2O) vapor.
9. The process as in any of the previous claims, wherein the second precursor flow comprises a gaseous source for oxygen.
10. The process as in any of the previous claims, comprising a glass substrate.
11. Apparatus (3) for aerosol-assisted process for depositing a coating (2) on a substrate (1), comprising:

a. a first conduit (6) for a first precursor flow leading into the deposition chamber (5),
b. a second conduit (9) for a second precursor flow leading essentially into the deposition chamber (5),
c. a first atomizer (7) for generating droplets (8) from at least one liquid precursor and leading into first conduit (6), and
d. a second atomizer (7*) for generating droplets (8*) from a precursor which is not the same as the liquid precursor used in the first atomizer (7).

12. An apparatus as specified in claim 11, comprising means (20) for directing the sprays from first atomizer (7) and second atomizer (7*) essentially towards each other.
13. An apparatus as specified in claims 11-12, comprising means for charging the droplets (8, 8*).
14. An apparatus as specified in claims 11-13, comprising means for widening the aerosol spray pattern by gas sprays.
15. Use of an apparatus as specified in claim 11, characterized in that no oxygen-containing material is fed into first conduit (6).
16. Use of an apparatus as specified in claim 11, characterized in that the gas used for the atomization contains fluorine.
17. Use of an apparatus as specified in claim 14, characterized in that the gas used in the gas sprays contains fluorine.

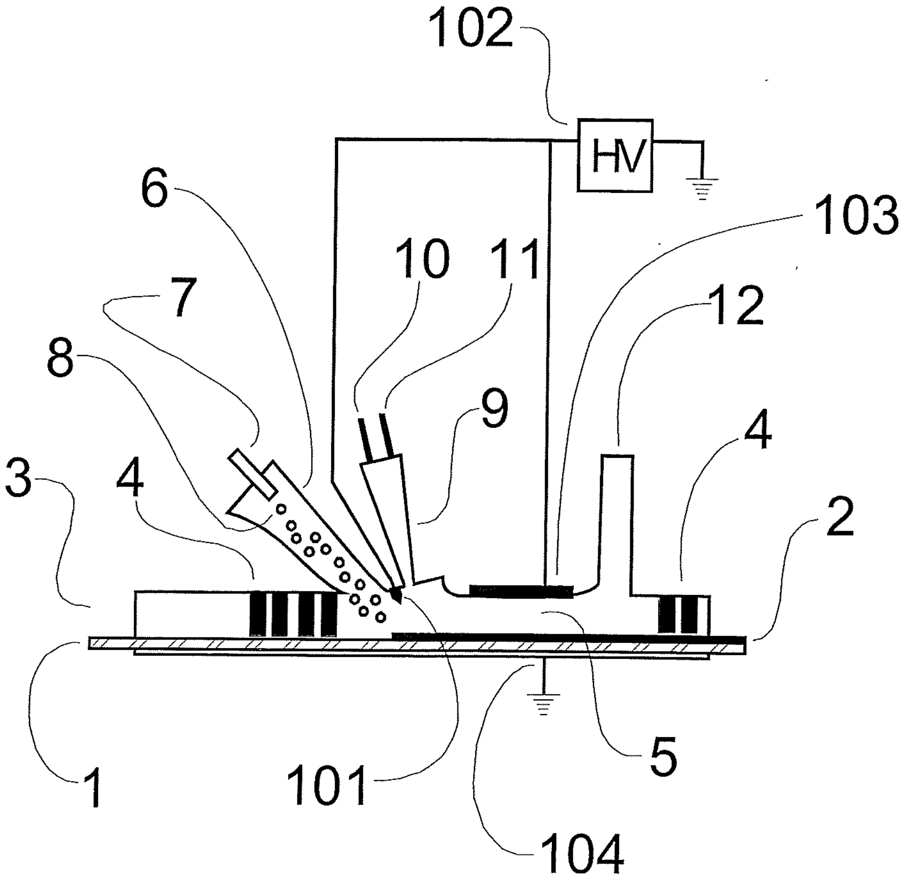

Fig. 1

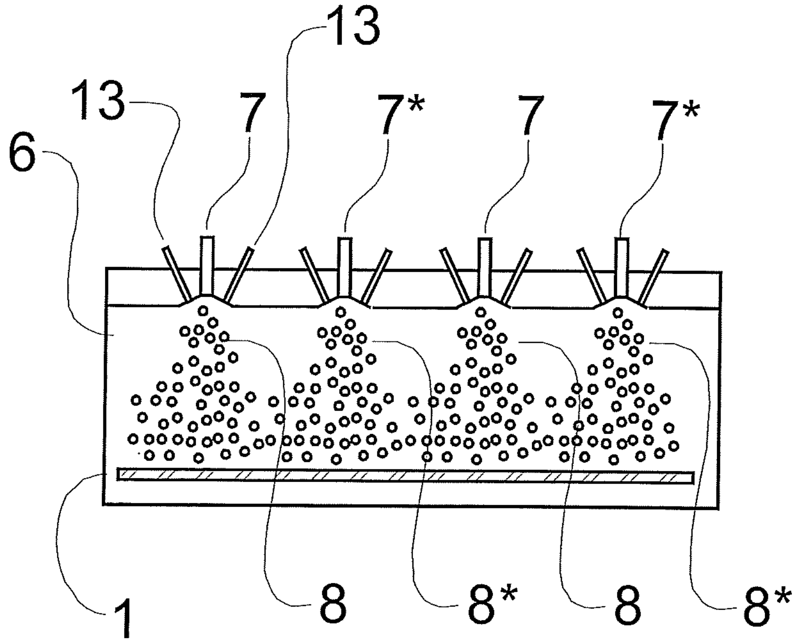

Fig. 2

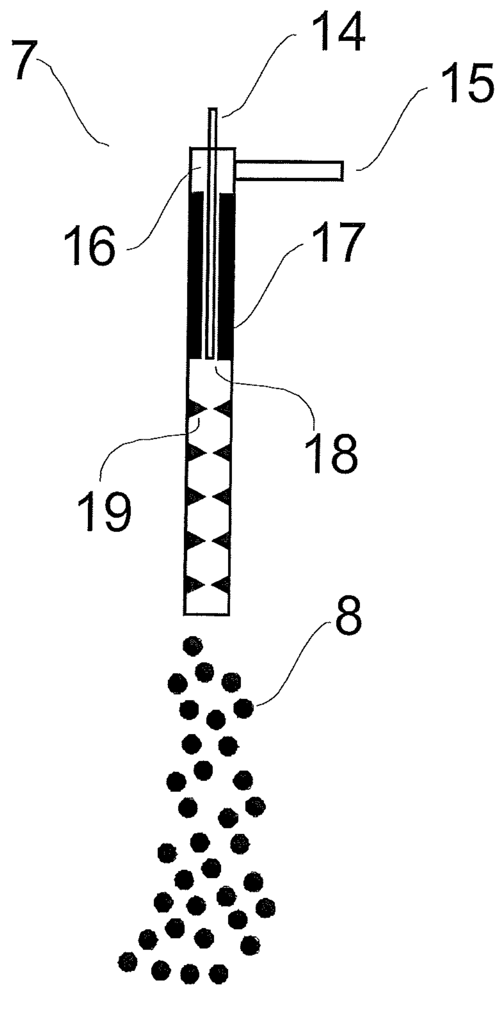

Fig. 3

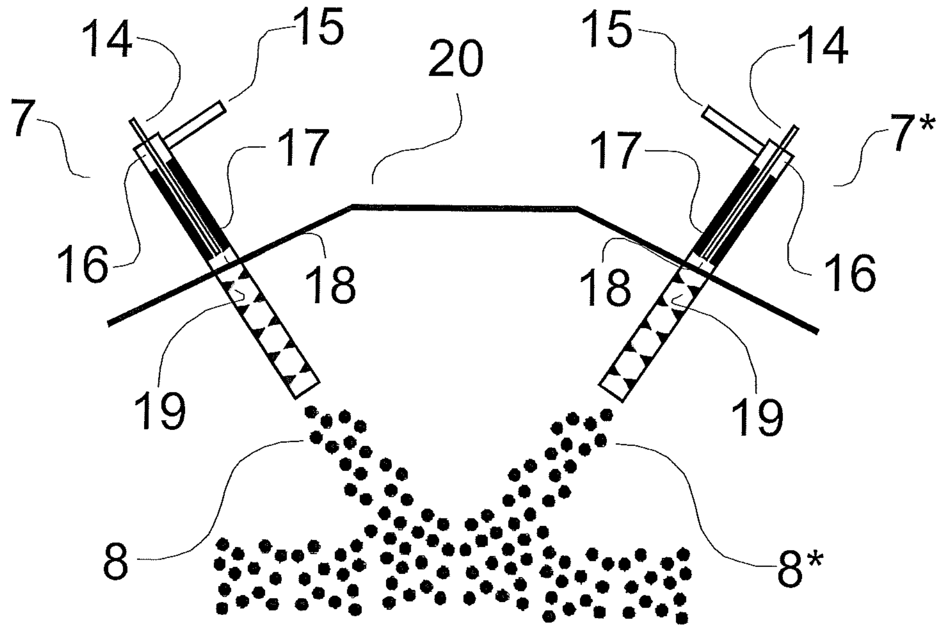

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2012/050219

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: B05D, B05C, B05B, C23C, H01L, C03C

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

FI, SE, NO, DK

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

EPO-Internal, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2010035312 A1 (TOSHIBA MITSUBISHI ELEC INC et al.) 01 April 2010 (01.04.2010)	11, 15
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"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

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Date of the actual completion of the international search	Date of mailing of the international search report
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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CLASSIFICATION OF SUBJECT MATTER

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C23C 16/448 (2006.01)
C23C 16/455 (2006.01)