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(71) **Applicant** *(for all designated States except US)*: **HELIANTHOS B.V.** [NL/NL]; Westervoortsedijk 71, NL-6827 AV Arnhem (NL).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **LENSSEN, Jozef** [NL/NL]; Landgraafstraat 31, NL-6845 EA Arnhem (NL). **SCHLATMANN, Rutger** [NL/DE]; Landauer Strasse 15, 14197 Berlin (DE).

(74) **Agents**: **ZONNEVELD, Hendrik Jan** et al.; Overschiestraat 180, NL-1062 XK Amsterdam (NL).

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(54) Title: VAPOUR DEPOSITION PROCESS AND DEVICE

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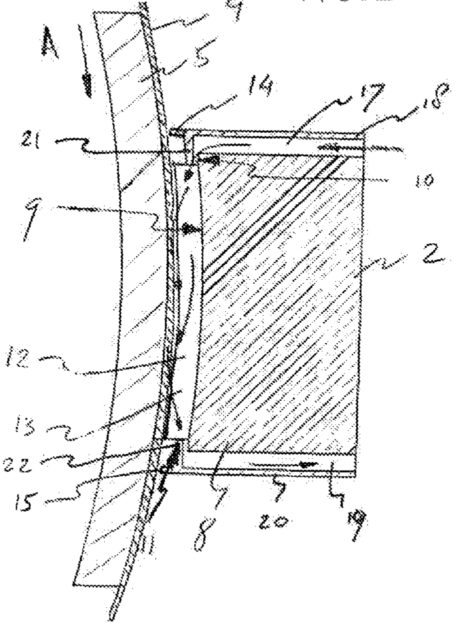


(57) **Abstract**: A vapour deposition process and a device for applying a deposit on a foil substrate (4) by chemical vapour deposition wherein a flow of precursor gases in a reaction chamber (12) is guided over the substrate, and wherein the reaction chamber is formed by a gap (12) between a curved surface (5) supporting the substrate (4), and a guiding surface (9), wherein the gas flows through the gap (12) from a slit shaped precursor gas inlet (10) to a slit shaped outlet (11), the inlet and the outlet having a width corresponding to the width of the reaction, chamber.

Vapour deposition process and device

The present invention relates to a vapour deposition process, in particular for the manufacture of foil or web material provided with a deposited film, such as a photovoltaic foil.

Chemical Vapour Deposition (CVD) involves the chemical reactions of gaseous reactants on or near a substrate, typically in a reaction chamber. Generally, gaseous precursors are supplied into a reaction chamber to undergo gas phase reactions forming intermediate species. At a high temperature above the decomposition temperatures of intermediate species inside the reactor, homogeneous gas phase reaction can occur where the intermediate species undergo subsequent decomposition and/or chemical reaction to form a dense layer and volatile by-products in the gas phase. The volatile by-products are discharged from the reaction chamber. At temperatures below the dissociation of the intermediate phase, diffusion or convection of the intermediate species can occur across the boundary layer, which is a thin layer close to the substrate. The gaseous precursors form intermediate species which are adsorbed onto the substrate. The adsorbed intermediate species diffuse along the surface before they finally react, and the deposit constituents are built into the structure forming the deposit. Gaseous by-products and unreacted gaseous precursor are removed from the boundary layer through diffusion or convection and extracted from the reaction chamber.

A wide variety of CVD processes exist. These CVD processes can differ in the applied pressure conditions. A distinction is made between atmospheric pressure CVD (APCVD) on the one hand and low-pressure CVD (LPCVD) on the other.

In the field of semi-conductors and photovoltaic devices, CVD is typically used to apply thin films of metal oxides, silicon oxides, metals, fluorides, nitrides, silicon nitrides, oxynitrides, semiconducting materials, such as silicon and/or germanium, compound semiconductors or mixtures thereof.

WO 98/13882 discloses a process for the manufacture of photovoltaic foils, e.g., by using a roll-to-roll process. One or more of the layers can be applied by using a CVD process, such as a transparent silica layer, a diffusion barrier layer, and/or a transparent conductive oxide layer, e.g., of indium tin oxide, cadmium sulfide or oxide, tin oxide (e.g., fluorine doped) or zinc oxide, which can for example be aluminum doped or boron doped.

US 3,198,167 discloses a roll-to-roll process for the production of metal coated decorative paper. A paper substrate is lead through an annular chamber between a cylindrical drum and an outer jacket. A flow of metal bearing gas flows over the paper substrate via a metal plating zone. The gas is supplied at three different points, resulting in a non-homogenous gas flow and uneven layer thickness of the deposited material on the substrate.

The object of the present invention is to come to a deposition process and a corresponding device allowing the formation of more even layer thicknesses and stable boundaries.

The object of the invention is achieved with a vapour deposition process for applying a deposit on a foil substrate by chemical vapour deposition wherein a flow of precursor gases in a reaction chamber is guided over the substrate, and wherein the reaction chamber is formed by a gap between a curved surface supporting the substrate, and a guiding surface, wherein the gas flows through the gap from a slit shaped precursor gas inlet to a slit shaped outlet, the inlet and the outlet having a width corresponding to the width of the reaction chamber. It has been found that this enables optimization of laminar flow substantially improving deposition stability. A very stable, laminar gas flow can be obtained resulting in a very constant thickness of the deposit layer and stable boundaries. In this context, the slits and the gap are considered to be of a corresponding width if any variation in width is too small to contribute to a flow disturbance that might negatively affect the uniformity of the layer thickness of the deposited layer to a noticeable extent.

The curved surface can, e.g., be the surface of a stationary cylindrical drum or a rotatable drum or roller.

Passing the outlet, the discharged gas can be guided away from the substrate, e.g. via an exhaust, to prevent that residual precursor gas will continue to be deposited on the substrate after passing the reaction chamber, in an uncontrolled manner.

The guiding surface can, e.g., be congruent with the opposite section of the curved surface. This way, a well defined gap can be obtained having a uniform width at least in the radial direction relative to the curved surface. Optionally, the width of the gap is also uniform in axial direction. In this context, the width is considered to be uniform if any variations in width are too small to disturb the laminar flow of the gas in such way that the uniformity in thickness of the deposited layer is affected to a noticeable extent.

The inlet can for example be defined by an edge of the guiding surface and a rib or strip located between the guiding surface and the curved surface. This way, the gas flow coming from the supply is deflected passing the inlet slit into a flow direction parallel to the guiding surface. This enables further optimization of laminar gas flow. The rib can form an integral part of the wall of the supply channel. The outlet slit can be defined in a similar arrangement.

The gap can be shielded by side walls and/or end walls to reduce the risk of unintentional outflow of precursor gases or volatile by-products. This risk can be further reduced by drawing ambient air into the reaction chamber, so that the exhaust flow will be larger than the supply flow of precursor gases. The distance between the curved surface and the congruent guiding surface can be adjusted to the desired through-flow and residence time of the precursor gases.

Optionally, the gap can widen or narrow down in flow direction of the precursor gases, e.g., gradually with about 10 % or less.

In a specific embodiment, the precursor gases can be guided to flow in tangential direction relative to the curved surface. To that end, the reaction chamber can for example comprise at two opposite ends of the guiding plate a precursor gas inlet and a gas flow outlet, respectively, the outlet and the inlet forming slits which are substantially parallel to the cylindrical axis of the curved surface.

Good deposit films are obtained if the foil is transported in a direction opposite to the flow direction of the precursor gases. Alternatively, the substrate can be transported into the same direction as the flow direction of the precursor gases in the reaction chamber.

To catalyze the reaction between the precursor gases, the foil can be heated, e.g., by one or more heating elements in the interior of the curved surface.

If so desired, the device according to the invention can comprise a series of two or more reaction chambers, e.g., in serial or parallel arrangement, facing different sections of the same curved surface. The reaction chambers can for instance be used for depositing different layers or different deposition materials.

In a specific embodiment, the reaction chambers can span less than 20 %, e.g., less than 12 %, e.g., less than 8 % of the circumference of the curved surface.

The CVD device according to the present invention can have one or more of the reaction chambers which are positioned with their open end making an angle with the horizontal. The angle can for example range between -60 to 60 degrees, more particularly between -45 to 45 degrees, e.g., between -30 to 30 degrees.

The invention is further explained with reference to the drawings, wherein:

Figure 1:	shows schematically a cross section of a device according to the invention;
Figure 2:	shows in cross section a reaction chamber of the device of Figure 1.

Figure 1 shows in cross section a device 1 for applying a deposition film on a foil substrate by chemical vapour deposition, in particular by an APCVD process. The device 1 comprises three deposition units 2 having an open end 3 directed to a foil substrate 4. The foil 4 is wound around a rotating drum or turner roller 5 formed by a cylindrical mantle 6 of a heat conductive material, such as a corrosion resistant steel. In the interior of the drum 5, five stationary heaters 7 are arranged to heat the mantle 6. In other embodiments, the number of heaters can be less or higher, if so desired. A large number, e.g., 200 or more, of smaller heater elements can for example be used to achieve uniform heat distribution.

The deposition units 2 are positioned with their open end 3 making an angle with the horizontal. Where the middle unit is under a right angle with the horizontal, the other two are under an angle of +45 and - 45 degrees with the horizontal, respectively.

Figure 2 shows more detail of a deposition unit 2 in cross section. The drum 5 rotates in the direction indicated by arrow A. The deposition unit 2 is provided with a guiding member 8 with a guiding surface 9 congruent to the opposite surface section of the drum 5. At one end of the guiding surface 9 the deposition unit 2 comprises a slit shaped inlet 10 for the supply of a precursor gas via a supply channel 17. The supply channel 17 is defined by one side of the guiding member 8 and a wall 18 which is parallel to the side of the guiding member 8. At the opposite end the deposition unit 2 comprises an outlet 11, which is also slit shaped and which is parallel to the inlet 10. The outlet 11 leads to an exhaust 19 leading the gas flow away from the substrate 4 and the curved surface 5. The exhaust 19 is defined by one side of the guiding member 8 and a wall 20 which is parallel to the side of the guiding member 8. The inlet 10 and the outlet 11 form slits parallel to the axis of the drum 5. Between the guiding surface 9 and the foil substrate 4 is a gap 12 forming a reaction chamber for the APCVD process. The gap 12 is confined by side walls 13, a first end wall 14 close to the inlet 10, and a second end wall 15 close to the outlet 11.

In the embodiment shown, the wall 18 and the first end wall 14 form a single plate carrying an inwardly extending rib 21 defining the inlet slit 10 in cooperation with an adjacent edge of the guiding surface 9. This way, gas flowing from the gas supply 17, is deflected by rib 21 to a flow direction parallel to the substrate 4 and the guiding surface 9. The cross sectional flow-through area of gas supply 17 is larger than the flow-through opening in the inlet slit 10.

Similarly, the wall 20 and the second end wall 15 form a single plate carrying an inwardly extending rib 22 defining the outlet slit 11 in cooperation with an adjacent edge of the guiding surface 9. The cross sectional flow-through area of the exhaust 19 is larger than the flow-through opening in the outlet slit 11.

Precursor gases flow in the direction indicated by the arrows in Figure 2. The heaters 7 heat the mantle 6 of the curved surface 5. The heated mantle 6 heats the foil substrate 4. As a result, the precursor gases near the substrate react and a film is deposited on the foil substrate.

In this embodiment, the roller rotates in the same direction as the tangential precursor gas flow. Alternatively, the rotational direction A of the roller can be opposite to the flow direction of the precursor reactant gases.

CLAIMS

1. A vapour deposition process for applying a deposit on a foil substrate (4) by chemical vapour deposition wherein a flow of precursor gases in a reaction chamber (12) is guided over the substrate, and wherein the reaction chamber is formed by a gap (12) between a curved surface (5) supporting the substrate (4), and a guiding surface (9), wherein the gas flows through the gap (12) from a slit shaped precursor gas inlet (10) to a slit shaped outlet (11), the inlet and the outlet having a width corresponding to the width of the reaction chamber.

2. Deposition process according to claim 1 wherein the discharged gas passing the outlet is guided away from the substrate.

3. Deposition process according to claim 1 or 2 wherein the substrate is a foil substrate and the curved surface is part of a drum (5), e.g., a rotatable drum.

4. Deposition process according to any one of the preceding claims wherein the gap (12) forming the reaction chamber is a gap of constant width.

5. Deposition process according to any one of the preceding claims wherein the precursor gases are guided to flow in a laminar flow in tangential direction relative to the curved surface (5).

6. Deposition process according to any one of the preceding claims wherein the substrate (4) is transported in a direction opposite to the flow direction of the precursor gases.

7. Deposition process according to any one of the preceding claims wherein the substrate (4) is heated by the curved surface.

8. Device for applying a deposition film on a substrate (4) in a roll-to-roll process by vapour deposition, the device comprising a curved surface and one or more reaction chambers formed by a gap (12) between a section of the curved surface (5) and a guiding surface (9), and wherein the one or more reaction chambers comprise a precursor gas inlet at one end of the guiding plate and an outlet at the opposite end, the outlet and the inlet forming slits of a width corresponding to the width of the reaction chamber.

9. Device according to claim 8 wherein the curved surface is cylindrical and wherein the slits of the outlet and the inlet are parallel to the cylinder axis of the curved surface.

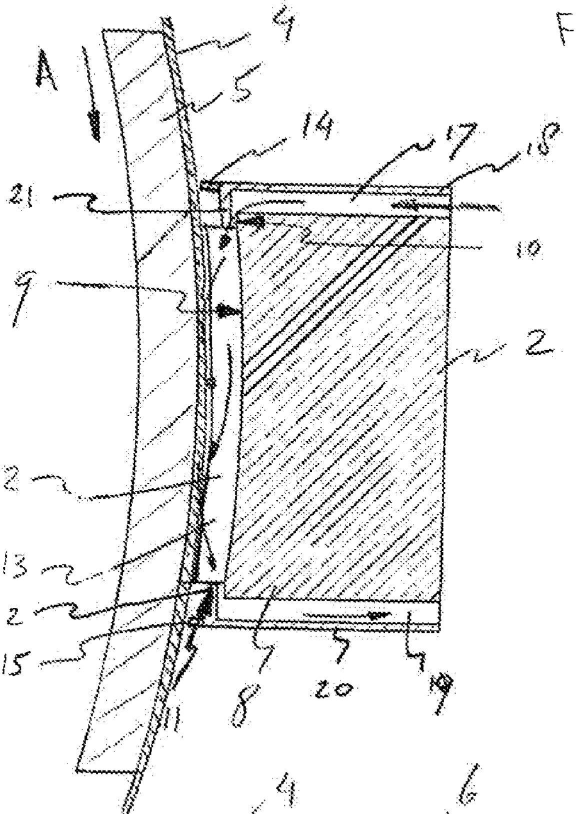
10. Device according to claim 8 or 9 wherein the outlet slit leads to an exhaust channel (19) having the same width as the outlet slit, which exhaust channel leads away from the curved surface.

11. Device according to any one of claims 8 - 10, wherein the inlet and/or the outlet are defined by an edge of the guiding surface (9) and a rib (21, 22) located between the guiding surface and the curved surface.

12. Device according to any one of claims 8 - 11, wherein the curved surface encases one or more heater elements.

13. Device according to any one of claims 8 - 11, wherein the gap forming the reaction chamber is bordered by one or more lateral and/or end partitions.

14. Device according to any one of the preceding claims 8 - 12, wherein a series of two or more reaction chambers is positioned in a serial arrangement over the same curved surface.



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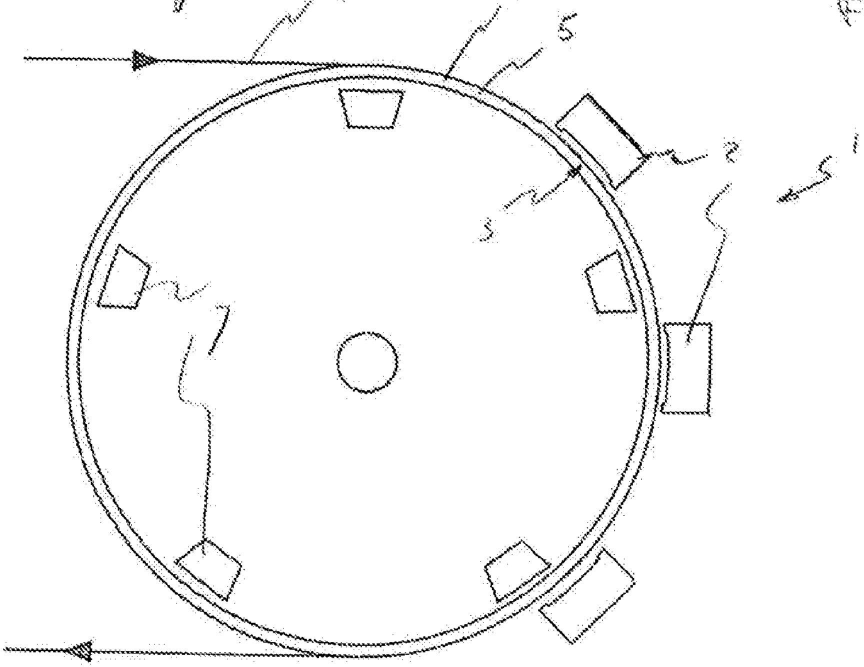

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/055997

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/54 C23C16/455

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

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 19 August 2009	Date of mailing of the international search report 26/08/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Ekhult, Hans

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/055997

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No
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