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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
02 November 2017 (02.11.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/188947 A1

(51) International Patent Classification:
C23C 16/50 (2006.01) *C23C 16/40* (2006.01)
C23C 16/455 (2006.01) *H01L 51/50* (2006.01)
C23C 16/54 (2006.01) *H01L 33/50* (2010.01)
C23C 16/34 (2006.01)

(21) International Application Number:
PCT/US2016/029621

(22) International Filing Date:
27 April 2016 (27.04.2016)

(25) Filing Language: English

(26) Publication Language: English

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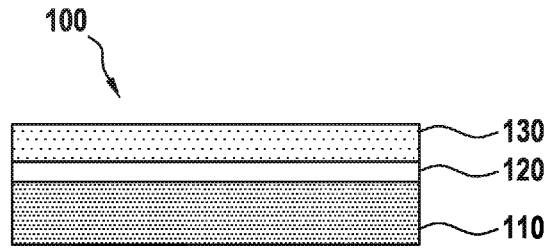
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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, 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,

(54) Title: SYSTEM FOR ATOMIC LAYER DEPOSITION ON FLEXIBLE SUBSTRATES AND METHOD FOR THE SAME

Fig. 1



(57) Abstract: A processing apparatus for atomic layer deposition of a thin film on a flexible substrate is described. The processing apparatus comprises a substrate support configured to continuously transport the flexible substrate. The processing apparatus further comprises a plurality of first gas distribution enclosures arranged opposite to a substrate front side for deposition of a first precursor material and a plurality of second gas distribution enclosures arranged opposite to the substrate front side for deposition of a second precursor material, wherein the plurality of first gas distribution enclosures and the plurality of second gas distribution enclosures are arranged alternatingly.

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MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, 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))*

SYSTEM FOR ATOMIC LAYER DEPOSITION ON FLEXIBLE SUBSTRATES AND METHOD FOR THE SAME

TECHNICAL FIELD

[0001] Embodiments of the present disclosure relate to an apparatus for depositing a layer stack including deposition by atomic layer deposition (ALD) on flexible substrates, a barrier layer stack, and methods of depositing layer stacks including deposition by atomic layer deposition (ALD) onto a flexible substrate and generating a barrier layer stack. Embodiments of the present disclosure further relate to a roll-to-roll processing apparatus configured to continuously transport the flexible substrate and to contact the flexible substrate on the back side thereof. Embodiments of the present disclosure particularly relate to a method for encapsulating a quantum dot layer stack.

BACKGROUND

[0002] Barrier films are utilized in applications where materials require very low ingress of moisture and/or oxygen. Barrier films are utilized for television screens, computer monitors, mobile phones, other hand-held devices, etc. for displaying information. For example, such devices can be organic light emitting diodes (OLED). A typical OLED may include layers of organic material situated between two electrodes that are all deposited on a substrate in a manner to form a matrix display panel having pixels that can be individually energized.

[0003] A new type of display technology is the quantum dot (QD) display type. Quantum dots can provide an alternative for commercial display technology. Quantum dots can support large, flexible displays but would not degrade as readily as OLEDs, making them appropriate candidates for screens such as flat-panel TVs, digital cameras, or mobile phones. Quantum Dot Enhancement Films (QDEF), are optical film components for LED driven LCD displays.

[0004] Besides the 30% to 50% less power consumption than LCDs, 50-100 times brighter illumination than cathode ray tube (CRT) displays, better saturated red and green colors, and the use of the same material to generate different colors, QD LEDs provide the advantage of manufacturability on polymer substrates.

[0005] Typical applications for barrier films are OLED films on flexible substrates, quantum dot enhancement films (QDEF) on flexible substrates for LCD displays, transparent food packaging, medical packaging, or organic photovoltaics. The display industry, particularly the OLED and/or the QD industry, as well as other industries that utilize substrate processing techniques, encapsulate moisture- or oxygen- sensitive devices to protect them from ambient moisture exposure.

[0006] ALD is a modified CVD process for the deposition of thin films by two or more self-limiting surface reactions. ALD employs chemisorption techniques to deliver precursor molecules on a substrate surface in sequential cycles. The cycle exposes the substrate surface to a first precursor and then to a second precursor. Optionally, a purge gas may be introduced between introductions of the precursor materials. The first and second precursors react to form a product compound as a film on the substrate surface. The cycle is repeated to form the layer to a predetermined thickness.

[0007] One method of performing ALD is by Time-Separated (TS) pulses of precursor gases in one deposition chamber. TS-ALD has several advantages over other methods; however one drawback of TS-ALD is that each surface exposed to the precursors, for example the interior of the chamber, will be coated with deposition. If these deposits are not removed periodically, the deposits will tend to flake and peel off eventually, leading to particulates ending up on the substrate and hence degraded moisture barrier performance of the deposited layer. If there is no effective way to clean the undesired deposits from the chamber surfaces in situ, then those chamber surfaces can be removed for cleaning "off-line".

[0008] Another method of performing ALD is providing separated deposition chambers for each precursor, known as Spatially Separated ALD (SS-ALD). To form a layer of predetermined thickness, the substrate gets alternatingly processed in the first and second deposition chamber. The cycle is repeated until the layer of a predetermined thickness has been formed.

[0009] Further improvements for performing ALD layers, e.g. on continuously transported large-scaled substrates are desired.

SUMMARY

[0010] In light of the above, a processing apparatus for atomic layer deposition of a thin film on a flexible substrate, a barrier layer stack deposited onto a flexible substrate, a method for depositing a barrier film on a flexible substrate, and a method for encapsulating a quantum dot structure are provided. Further aspects, advantages, and features of the present disclosure are apparent from the description, and the accompanying drawings.

[0011] According to one embodiment, the processing apparatus for atomic layer deposition of a thin film on a flexible substrate is provided. The apparatus includes a substrate support configured to continuously transport the flexible substrate, a plurality of first gas distribution enclosures arranged opposite to a substrate front side for providing a first precursor material on the front side of the flexible substrate, and a plurality of second gas distribution enclosures arranged opposite to the substrate front side for providing a second precursor material on the front side of the flexible substrate, wherein the plurality of first gas distribution enclosures and the plurality of second gas distribution enclosures are arranged alternatingly.

[0012] According to another embodiment a roll-to-roll processing apparatus for atomic layer deposition of a thin film on a flexible substrate is provided. The roll-to-roll processing apparatus includes a winding system for transporting said flexible substrate from an unwinding roller to a re-winding roller, a substrate support configured to continuously transport the flexible substrate and to contact the flexible substrate on a back side thereof, a plurality of first gas distribution enclosures arranged opposite to a substrate front side for deposition of a first precursor material, a plurality of second gas distribution enclosures arranged opposite to the substrate front side for deposition of a second precursor material, wherein the plurality of first gas distribution enclosures and the plurality of second gas distribution enclosures are arranged alternatingly, at least one gas separation stage arranged between at least one first gas distribution enclosure of the plurality of first gas distribution enclosures and at least one second gas distribution enclosure of the plurality of second gas

distribution enclosures, and an excitation unit coupled to the at least one first or second gas distribution enclosure configured to induce a chemical reaction, wherein the excitation unit is a plasma source.

[0013] According to another embodiment, a barrier layer stack deposited onto a flexible substrate is provided. The barrier layer stack includes at least one barrier layer deposited by atomic layer deposition followed by at least one barrier layer deposited by plasma-enhanced chemical vapor deposition having an overall thickness of at least 50 nm, for example 120 nm or more.

[0014] According to a yet further embodiment, a method for depositing a barrier film on a flexible substrate is provided. The method includes continuously transporting a flexible substrate from an unwinding roller to a re-winding roller, contacting the flexible substrate on the back side thereof, depositing a first precursor material on the flexible substrate in a first gas distribution enclosure arranged opposite to the substrate front side, depositing a second precursor material on the flexible substrate in a second gas distribution enclosure arranged opposite to the substrate front side, forming a product compound by a chemical reaction of the first precursor material and the second precursor material, generating a barrier layer stack by repeating the deposition of the first precursor material and the second precursor material on the flexible substrate, and depositing a layer by plasma-enhanced chemical vapor deposition over the barrier layer stack.

[0015] According to a yet another embodiment, a method for encapsulating a quantum dot structure is provided. The method includes continuously transporting a flexible substrate, depositing a first precursor material on the flexible substrate in a first gas distribution enclosure arranged opposite to the substrate front side, depositing a second precursor material on the flexible substrate in a second gas distribution enclosure arranged opposite to the substrate front side, forming a product compound by a chemical reaction of the first precursor material and the second precursor material, generating a barrier layer stack by repeating the deposition of the first precursor material and the second precursor material on the flexible substrate, depositing a layer by plasma-enhanced chemical vapor deposition over the barrier layer stack to form a quantum dot encapsulation layer stack, and encapsulating one or more quantum dot structures with the quantum dot encapsulation layer stack.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to embodiments. The accompanying drawings relate to embodiments of the disclosure and are described in the following:

FIG. 1	shows a cross-sectional view of a layer stack according to embodiments described herein;
FIG. 2	shows a schematic depiction of an ALD reaction cycle according to embodiments described herein;
FIGS. 3a, 3b	show a schematic view of first and second gas distribution enclosures according to embodiments described herein;
FIG. 4	shows images of test samples according to embodiments described herein;
FIGS. 5a, 5b	show analysis results of test samples according to embodiments described herein;
FIG. 6	shows a schematic view of a roll-to-roll processing apparatus according to embodiments described herein;
FIG. 7	shows a schematic view of a roll-to-roll processing apparatus according to embodiments described herein;
FIG. 8	shows a cross-sectional view of a quantum dot encapsulation according to embodiments described herein;
FIG. 9	shows a cross-sectional view of a quantum dot encapsulation according to embodiments described herein;
FIG. 10	shows a flow chart illustrating a method for depositing a barrier layer on a flexible substrate according to embodiments described herein; and

FIG. 11 shows a flow chart illustrating a method for encapsulating a quantum dot structure according to embodiments described herein.

DETAILED DESCRIPTION

[0017] Reference will now be made in detail to the various embodiments of the disclosure, one or more examples of which are illustrated in the figures. Within the following description of the drawings, the same reference numbers refer to same components. Generally, only the differences with respect to individual embodiments are described. Each example is provided by way of explanation of the disclosure and is not meant as a limitation of the disclosure. Further, features illustrated or described as part of one embodiment can be used on or in conjunction with other embodiments to yield yet a further embodiment. It is intended that the description includes such modifications and variations.

[0018] A thin conformal layer of material is beneficial as a means of reducing Water Vapor Transmission Rate (WVTR) through encapsulation layer(s). High performance barrier films can be defined as having WVTR < $1x10^{-3}$ g/m²/day, with some applications requiring as low as $1x10^{-6}$ g/m²/day.

[0019] There are a number of commercial ways to encapsulate devices. According to some embodiments described herein, an ALD process to cover a moisture-sensitive device is provided. Plasmaless atomic layer deposition can denote an ALD process for which no plasma is produced for forming a solid layer. Depending on the precursor gases, it may be beneficial to induce the chemical reaction by excitation of a precursor gas. Plasma-enhanced atomic layer deposition can denote an ALD method in which the second precursor (starting compound) is fed with a plasma being simultaneously produced. Alternatively, temperature-enhanced atomic layer deposition can denote an ALD method in which the precursor gases are fed during being simultaneously heated.

[0020] Substrates such as PET (polyethylene terephthalate), PEN (polyethylene naphthalate), or PI (polyimide) are used, followed by a sequence of thin films which act as a

barrier, for example a water vapor barrier or a gas barrier. Plasma-enhanced chemical vapor deposited (PECVD) layers such as SiN_x or SiO_2 are often used as barrier layers due to their high deposition rates (>100nm/min) and low ideal WVTR (< $1x10^{-7}$ g/m²/day). However, defects in the films lead to much higher WVTR in practice due to particles on the substrate surface, defects in the substrate, and/or grain boundaries in the film. PECVD layer thicknesses are typically in the 100nm – 1μm range. Rather than covering any defects on the substrate surface with the layer, the defects typically propagate through the film, leading to increased local WVTR.

[0021] Atomic layer deposition (ALD) is also used for barrier layers such as Al_2O_3, TiO_2, ZrO_2, SiO_2, HfO_x, and others, and combinations thereof. An advantage of ALD is a high-quality, conformal film, leading to very low WVTR. As compared to PECVD, ALD deposition rates are typically very low (< 2 nm/min). For example, film thicknesses can be several tens of nanometers such as 20 nm, 30 nm, or 40 nm, wherein a limitation may exist e.g. due to a reasonable production time. With these thicknesses, ALD layers can for example be disrupted by larger particles, especially those that may detach from the surface, leaving a void with high WVTR.

[0022] According to embodiments of this disclosure, an ALD starting layer is deposited prior to PECVD deposition to decrease the number of defects in the barrier film. A mechanism for this improvement can be that the ALD starting layer provides a defect-free surface for the PECVD deposition. This defect-free surface provides fewer defects to propagate through the subsequent deposited PECVD layer. Defects in the SiN layer can be subject to hydrolysis at high temperature and/or humidity conditions. According to some embodiments, the ALD layer can acts as a buffer layer or a seed layer to prevent contact between water vapor diffusing through the plastic substrate and the SiN_x layer deposited thereon.

[0023] According to an embodiment of the present disclosure as illustrated in FIG. 1, a barrier structure can include a barrier layer 120 deposited by ALD onto a flexible substrate 110. The barrier layer 120 deposited by ALD can be a layer stack comprising several mono-layers formed of a product compound by a chemical reaction of a first precursor material and a second precursor material. The barrier layer stack deposited by ALD can have a thickness of 3 nm or above. According to another embodiment, the barrier layer stack deposited by

ALD can have a thickness of 20 nm or below. According to yet a further embodiment, the barrier layer stack deposited by ALD can have a thickness of 3 nm or above and of 20 nm or below. Over this ALD barrier layer stack, a layer by plasma-enhanced chemical vapor deposition (PECVD layer 130) is deposited. The barrier layer stack includes at least one barrier layer deposited by atomic layer deposition followed by a PECVD layer e.g. having an overall thickness of at least 50 nm or above, particularly of 100 nm or above, more particularly of 500 nm or above.

[0024] According to embodiments described herein, FIG. 2 illustrates a process of forming a product compound by a chemical reaction of the first precursor material and the second precursor material. The product compound can be formed on the flexible substrate 110 during transportation of the flexible substrate. In a first gas distribution enclosure 150 arranged opposite to the substrate front side as illustrated in FIGS. 3a and 3b, the first precursor material A can be provided on the substrate surface by chemisorption. As illustrated in FIG. 2, during passage, the flexible substrate 110 is covered by an increasing number of particles of the first precursor A. In the first gas distribution enclosure 150, the flexible substrate 110 is provided with a layer, e.g. a closed layer, of particles of precursor A.

[0025] The flexible substrate 110 leaving the first gas distribution enclosure 150 can be transported into the second gas distribution enclosure 160 as shown in FIGS. 3a and 3b. As illustrated in FIG. 2, during transportation of the flexible substrate through the second gas distribution enclosure, the second precursor material B can be provided by chemisorption on the substrate having a surface coated with a film of precursor A. In the second gas distribution enclosure 160, the flexible substrate 110 is provided with a layer, e.g. a closed layer, of particles of the precursors A and B.

[0026] By a chemical reaction, the deposited particles of precursors A and B can form a product compound AB. Depending on the nature and/or the combination of the first and second precursors A and B, the chemical reaction can autonomously start self-induced. It can be beneficial to promote or induce the chemical reaction by an excitation unit 140. The excitation unit 140 can be optionally installed in the first and/or second gas distribution enclosures. For example, the excitation unit can be a plasma source or a heater. For instance, the plasma can be generated from a precursor gas by a micro-wave antenna or by a RF antenna.

[0027] The substrate section passing the first and second gas distribution enclosures can be provided with a mono layer of the product compound AB. For forming a barrier layer by atomic layer deposition having a sufficient thickness, the substrate can be provided with several mono layers of the ALD product compound AB one above the other. An ALD layer stack of several mono layers can be generated by alternatingly passing a first gas distribution enclosure and second gas distribution enclosure. For each mono layer of product compound AB, a pair of first and second gas distribution enclosures can be passed. Beneficially, a plurality of first and second gas distribution enclosures can be arranged alternatingly.

[0028] The flows of the first and second precursor gases can be adapted to the transportation velocity of the flexible substrate. It is beneficial to saturate the surface quickly. With increasing saturation rate, the dimensions of the first and second gas distribution enclosures can be reduced. Reducing the dimensions of the gas distribution enclosures leads to smaller dimensions of the processing apparatus for atomic layer deposition. Reducing the dimensions of the processing apparatus leads to lower cost of ownership.

[0029] According to embodiments of the present disclosure, the precursors A can be selected from the group consisting of: Trimethylaluminum (TMA), Tetrakis(dimethylamido)Hafnium(IV) (TDMAHf), Tetrakis[EthylMethylAmino]Hafnium (TEMAHf), Tetrakis(dimethylamido)Zirconium(IV) (TDMAZr), tris(dimethylamino)silane (TDMAS), Titanium tetrachloride ($TiCl_4$), or Tetrakis(dimethylamino)Titanium (TDMAT). The first precursor materials such as metal precursors are typically very volatile, so thermal activation is sufficient. The second precursors B can be selected from the group consisting of: H_2O, H_2O_2, O_2, O_3, N_2O.

[0030] The second precursor material can be an oxidizer. For plasma-less ALD the oxidizer can be, e.g. water or O_3, which are thermally activated. In case of plasma-enhanced ALD, for example oxygen is injected into the second gas distribution enclosure as an oxidizer. An oxygen plasma can be ignited by a plasma source. The plasma source can be installed in the second gas distribution enclosure. The oxygen particles excited by the plasma can react with the first precursor material chemisorbed to the substrate surface.

[0031] According to embodiments described herein, FIGS. 3a and 3b illustrate a pair of first and second gas distribution enclosures. For generating an ALD barrier layer of

sufficient layer thickness, a plurality of first gas distribution enclosures 150 and a plurality of second gas distribution enclosures 160 can be arranged opposite to the substrate front side for deposition of a first and second precursor material, wherein the plurality of first gas distribution enclosures 150 and the plurality of second gas distribution enclosures 160 are arranged alternatingly.

[0032] Between at least one first gas distribution enclosure 150 of the plurality of first gas distribution enclosures and at least one second gas distribution enclosure 160 of the plurality of second gas distribution enclosures, a gas separation stage 170 can be arranged. The gas separation stage 170 can include a gas feeding unit 200 such as a gas lance for providing a purge gas or a separation gas between a first and a second gas distribution enclosure. The gas lance can have several gas outlet openings over the length of the lance, e.g. along a width of a flexible substrate or in a direction perpendicular to a substrate transport direction, for uniformly providing the purge gas or a separation gas over the width of the flexible substrate. The precursor gases A and B exiting the first and/or second gas distribution enclosures, respectively, can be evacuated by vacuum pumps arranged in the rear of the gas separation stages 170 as indicated by arrows 210.

[0033] The precursor gases A and B exiting the first and the second gas distribution enclosures, respectively, can be evacuated by vacuum pumps together with the purge gas or the separation gas. The purge gas or separation gas can reduce the concentration of precursor gases or dilute the precursor gases A and B such that a reaction can be avoided. Without a reaction of the precursor gases A and B, the components outside the first and second gas distribution enclosures can be kept free of depositions from product compound AB. Without such depositions, a pollution of installed components can be avoided.

[0034] According to the embodiment illustrated in FIG. 3a, the first and/or second precursor gases A and B can be fed into the first and/or second gas distribution enclosures as indicated by arrows 180. The precursor gases can pass a gas distribution plate 190, for example a shower head, for a uniform distribution of the precursor gas over the substrate surface. The gas distribution plate, e.g. the shower head, can be provided with a plurality of openings. The pressure of the precursor gases at the input side of the gas distribution plate, e.g. of the shower head, is according to some embodiments higher than at the deposition side

of the gas distribution plate, e.g. of the shower head, resulting in a pressure difference. For example, the pressure difference can be one order of magnitude.

[0035] According to an alternative embodiment as illustrated in FIG. 3b, the first and second gas distribution enclosures can each include a precursor gas feeding unit 220 arranged inside the housing of the gas distribution enclosures. One precursor gas feeding unit 220 can provide the first precursor gas into the first gas distribution enclosure. A second precursor gas feeding unit 220 can provide the second precursor gas into the second gas distribution enclosure. The precursor gas feeding units 220 can be gas lances, for example, having several gas outlet openings over the length. Further, the first and/or the second the gas distribution enclosures can be provided with an excitation unit 140. In FIG. 3b, the excitation unit 140 is shown in the second gas distribution enclosure 160. Alternatively or additionally, an excitation unit 140 can be provided in the first gas distribution enclosure 150.

[0036] According to an embodiment, the barrier layer stack can include at least one barrier layer deposited by atomic layer deposition followed by a PECVD layer. A PECVD layer such as SiN_x or SiO_2 can be used as a barrier layer. According to embodiments of this disclosure, the ALD barrier layer is deposited as a starting layer followed by the deposition of a PECVD layer. The ALD barrier layer can decrease the number of defects in the growing PECVD layer. A mechanism for this improvement can be that the ALD starting layer provides a defect-reduced or a defect-free surface for the PECVD deposition. This defect-reduced or defect-free surface provides fewer defects to propagate through the subsequent deposited PECVD layer.

[0037] Defects in the PECVD layer can be subject to hydrolysis at high temperature and/or humidity conditions. As a result of the hydrolysis, the WVTR increases, i.e. the effect of the barrier film decreases. According to embodiments described herein, the ALD barrier layer can act as a buffer layer to prevent contact between the water vapor diffusing through the plastic substrate and the PECVD layer deposited thereon. The buffer effectiveness of the ALD barrier layer can be demonstrated by an aging test in a chamber at environmental conditions of 85°C and 85%RH (relative humidity). In this aging test, the WVTR is detected.

[0038] A common method to quantify WVTR is the calcium test. For example, the calcium test is known from publication "Evaluating High Performance Diffusion Barriers:

the Calcium Test" by G. Nisato, PCP Bouten, PJ Slikkerveer, WD Bennett, GL Graff, N Rutherford, and L Wiese (Proc. Int. Display workshop/Asia Display, 2001/10/16, p. 1435-1438). The barrier layer stack is coated by a thin film of calcium (Ca) and then sealed to a glass lid with a getter-containing adhesive. The Ca layer starts as an opaque film having an optical transmission of, for example, about 10% for a 60nm Ca layer. As the Ca layer is exposed to water, there is a chemical reaction from Ca to $Ca(OH)_2$, which is transparent.

[0039] The Ca test provides the following data: from the optical transmission of the Ca layer at areas with no defects before starting the test, the thickness of the Ca layer can be calculated. Using the change in optical transmission, i.e. the change of thickness over time, the WVTR rate can be calculated. This is referred to as the "bulk permeation". If there are defects in the barrier layer stack, pinholes will appear in the Ca layer over time. Both the number density and area of these pinholes can be calculated over time. The Ca test data disclosed herein were generated according to test method A as described in the above mentioned publication.

[0040] The sample structures as shown in Table 1 were subjected to the Ca test:

Substrate	1st barrier layer	Thickness	2nd barrier layer	Thickness
PEN	TiO_2 (deposited by ALD)	20 nm	----------	----------
PEN	SiN_x (deposited by PECVD)	500 nm	----------	----------
PEN	SiN_x (deposited by PECVD)	500 nm	TiO_2 (deposited by ALD)	20 nm
PEN	TiO_2 (deposited by ALD)	20 nm	SiN_x (deposited by PECVD)	500 nm

[0041] FIG. 4 illustrates the images of the Ca test data for the four samples of Table 1 at different aging times. The samples were aged in an environmental chamber at a temperature of 85°C and a humidity of 85%RH. As can be seen from FIG. 4, the single layer samples present the highest WVTR. The TiO_2 layer (sample 1) presents defects in the barrier layer visualized by pinholes in the Ca layer. The decreasing areal optical density of the SiN_x

single layer (sample 2) indicates a high bulk permeation of water vapor. The lowest defect density presents sample 4 with the layer stack of a seed layer of TiO_2 deposited by ALD and a barrier layer of SiN_x deposited by PECVD.

[0042] The plot of FIG. 5a illustrates the analysis of the Ca area remaining for samples in FIG. 4. The Ca area begins at 100%, and decreases as the Ca area is exposed to water vapor. The sample with only SiN_x fails after approximately 150 h.

[0043] The plot of FIG. 5b illustrates the analysis of the number of defects for samples in FIG. 4, as evidenced by the appearance of pinholes in the Ca layer. Pinholes become detectible when the diameter exceeds 10um, as the pixel size of the images is approximately 3um. It is notable that for the TiO_2/SiN_x sample, there are very few defects when the sample is aged at >450 h.

[0044] Table 2 shows the performance metrics of FIGS. 5a and 5b for different barrier layer configurations, assuming an acceleration factor of 100x. The acceleration factor of 100x is based on the assumption that aging 100 hours at 85°C/85%RH is comparable to aging 10,000 hours at 20°C/50%RH. A WVTR of $2x10^{-5}$ g/m²/day is the detection limit for this apparatus. Error ranges are calculated from the standard deviation of at least three samples fabricated simultaneously.

Parameter	TiO_2 20nm	SiN_x 500nm	SiN_x+TiO_2 500nm+20nm	TiO_2+SiN_x 20nm+500nm
Time to 90% Ca area remaining (h)	200 ± 70	140 ± 30	290 ± 90	250 ± 100
WVTR (RT*) g/m²/day	$< 2x10^{-5}$	$5x10^{-5}$	$< 2x10^{-5}$	$< 2x10^{-5}$
Number of pinholes after 100h	28 ± 9	35 ± 4	7 ± 5	3 ± 1

[0045] The Ca test demonstrated that the performance of the PECVD barrier films was significantly improved by the incorporation of an ALD seed layer. Specifically, the number of defects in the barrier film was decreased significantly. The overall performance of the ALD/PECVD layer was significantly better than either material alone, or the common

structure consisting of PECVD/ALD. In effect, the ALD barrier layer is improving the quality of the subsequent PECVD barrier layer.

[0046] According to embodiments described herein which can be combined with other embodiments, synthetic substrate materials such as PET (polyethylene terephthalate), PEN (polyethylene naphthalate), or PI (polyimide) can be coated, for example, in roll-to-roll processing apparatuses. A roll-to-roll processing apparatus can include an unwinding chamber, a processing chamber, and/or a re-winding chamber. In some roll-to-roll processing apparatuses, unwinding and re-winding of the flexible substrate can be performed in a common winding chamber.

[0047] The processing chamber can include a plurality of transport rollers. The transport rollers can act as supports for a flexible substrate. A transport roller can be a processing drum such as a coating drum or a coating roller. The processing drum can provide a surface for contacting the backside of the flexible substrate. The surface of the processing drum can be kept at a predetermined temperature level. The processing region can be arranged adjacent to the front side of the traveling flexible substrate. A transport roller can further be a guide roller for deflecting the transport direction of the flexible substrate from a straight direction. The flexible substrate can be moved through a processing region by one or more guide rollers.

[0048] According to another embodiment, the flexible substrate may further be transported on several guide rollers providing a free-span path. Processing of the substrate, such as coating of the substrate can be provided at a free-span path. The free-span path may be a portion of the transportation path of the flexible substrate. Temperature adjustment devices such as heaters or radiation heaters can be provided in the free-span path facing the backside of the flexible substrate.

[0049] It is noted here that a flexible substrate or web as used within the embodiments described herein can typically be characterized in that the flexible substrate is bendable. The term "web" may be synonymously used with the term "strip", the term "tape", or the term "flexible substrate". For example, the web, as described in embodiments herein, may be a foil or another flexible substrate. However, as described in more detail herein, the benefits of embodiments described herein may also be provided for non-flexible substrates or carriers

of other inline deposition systems. Yet, it is understood that particular benefit can be utilized for flexible substrates and applications for manufacturing devices on flexible substrates.

[0050] In certain roll-to-roll processing apparatuses, the flexible substrate can be transported along a serpentine path around guiding rollers or deflection rollers spaced apart. This serpentine path configuration results in alternatingly contacting the front side and the back side of the flexible substrate by rollers when the flexible substrate moves through the system. Such a mechanical contact can interfere with the ALD process, as the mechanical contact can disturb the chemisorbed precursor or result in mechanical damage to the coating and/or underlying substrate surface. Typically, this damage can be caused by imperfections or particles on the surface of rollers, or by surface imperfections generated in the deposited ALD layer. The rollers contacting an already deposited ALD layer can press particles into the coated surface or can lift off sections of the deposited ALD layer. Such damages of the coated side of the substrate can reduce or compromise the barrier properties.

[0051] According to some embodiments of the present disclosure, in order to avoid the above described damages, the flexible substrate is transported by the transport rollers such that only the backside of the flexible substrate is contacted. All rollers are contacting only the backside of the flexible substrate. No roller contacts the front side of the flexible substrate.

[0052] FIG. 6 shows a schematic view of a roll-to-roll processing apparatus 225 according to embodiments described herein. The roll-to-roll processing apparatus 225 can be a vacuum deposition apparatus which can be evacuated by vacuum pumps (not depicted in FIG.6). The flexible substrate 110 can be transported from unwinding roller 230 via processing drum 240 to re-winding roller 250. A plurality of first gas distribution enclosures 150 and a plurality of second gas distribution enclosures 160 can be arranged opposite to the substrate front side for the deposition of a first and second precursor material A and B, respectively, wherein the plurality of first gas distribution enclosures 150 and the plurality of second gas distribution enclosures 160 are arranged alternatingly. The front side of the flexible substrate 110 is the coated side where the layer or layer stacks can be deposited. A contact of the front side of the flexible substrate 110 with any roller can be avoided to keep the deposited layers free of defects.

[0053] According to embodiments described herein, the plurality of first gas distribution enclosures 150 and the plurality of second gas distribution enclosures 160 can be arranged alternatingly in series or in a row. Accordingly, the plurality of first gas distribution enclosures 150 and the plurality of second gas distribution enclosures 160 are arranged alternatingly one after the other and between a rewinding roller, e.g. a first position, and a winding roller, e.g. a second position, for example along the path of a flexible substrate in a roll-to-roll processing apparatus. As illustrated in FIG. 6 and FIG. 7, the sequence of first and second gas distribution enclosures can be arranged alternatingly. The sequence of the alternatingly arranged plurality of first and second gas distribution enclosures provides the possibility to perform a plurality of ALD monolayers generated one above the other. The plurality of ALD monolayers provide an ALD layer of preselected layer thickness.

[0054] Referring back to FIG. 6, the processing drum can be provided with a tempering unit configured for tempering the flexible substrate (not shown in FIG. 6). Tempering the flexible substrate can be heating or cooling. The tempering unit can be provided with a control unit. The control unit provides the possibility to adjust the process temperature to a preselected temperature level. By tempering the flexible substrate, the deposition process can be adapted to the type of ALD process to be performed. For example, encapsulation of OLEDs or QD structures typically is usually performed at lower temperatures between 80°C and 110°C, so as not to damage either the underlying flexible substrate or OLED layer stack or QD structure.

[0055] Between at least one first gas distribution enclosure 150 of the plurality of first gas distribution enclosures and at least one second gas distribution enclosure 160 of the plurality of second gas distribution enclosures, a gas separation stage 170 can be arranged. The gas separation stage 170 can include a gas feeding unit 200 such as a gas lance for providing a purge gas or a separation gas between a first and a second gas distribution enclosure. The gas lance can have several gas outlet openings over the length for uniformly providing the purge gas or a separation gas over the width of the flexible substrate. The precursor gases A and B exiting the first and/or second gas distribution enclosures, respectively, can be evacuated by vacuum pumps arranged in the rear of the gas separation stages 170 as indicated by arrows 210.

[0056] According to embodiments described herein, the roll-to-roll processing apparatus 225 can be provided with at least one further deposition chamber. For example, the at least one further deposition chamber can be configured for plasma-enhanced chemical vapor deposition (PECVD). The PECVD deposition chamber 260 can include a plasma source 270. The PECVD deposition chamber 260 can be configured to deposit a PECVD layer onto the barrier layer or barrier layer stack deposited by ALD. For example, the PECVD layer can be a SiO_2 layer, a SiNx layer, or a SiN layer. The at least one deposition chamber configured for plasma-enhanced chemical vapor deposition (PECVD) can be the first deposition chamber in the direction of transport of the flexible substrate downstream of the plurality of first gas distribution enclosures and the plurality of second gas distribution enclosures. The depicted number and/or type of gas distribution enclosures or further deposition chambers is arbitrary and is not to be regarded as delimiting the scope of disclosure. According to an alternative embodiment, a PECVD layer can be deposited in a separate roll-to-roll deposition apparatus.

[0057] FIG. 7 shows a schematic view of another roll-to-roll processing apparatus according to embodiments described herein. The roll-to-roll processing apparatus 225 can be a vacuum deposition apparatus which can be evacuated by vacuum pumps (not depicted in FIG.7). The roll-to-roll processing apparatus 225 includes two separate chambers for unwinding and re-winding the flexible substrate 110. The unwinding chamber can be provided with unwinding roller 230. The re-winding chamber can be provided with re-winding roller 250.

[0058] The unwinding chamber and the re-winding chamber can be provided with a separate winding system for unwinding and re-winding an interleaf web or foil. The interleaf winding system is depicted with dotted lines in FIG. 7. The interleaf web or foil can protect the front side of the flexible substrate. Particularly, the barrier layers deposited onto the processed flexible substrate can be protected against damages.

[0059] The unwinding chamber and the re-winding chamber can be separated with a maintenance zone 280. The maintenance zone 280 provides space for an operator to access the unwinding and/or re-winding chambers for maintenance. For example during maintenance, a bale of processed flexible substrate can be exchanged by an empty re-

winding shaft. Further, an empty re-winding shaft can be exchanged by an uncoated bale of flexible substrate 110.

[0060] The roll-to-roll processing apparatus 225 of FIG. 7 can further provide two processing drums 240 and 240', respectively. The processing chamber comprising the two processing drums can be separated from the unwinding chamber and/or the re-winding chamber by load-lock valves 290. The flexible substrate 110 can be transported from unwinding roller 230 via processing drum 240 and processing drum 240' to re-winding roller 250. A plurality of first gas distribution enclosures 150 and a plurality of second gas distribution enclosures 160 can be arranged opposite to the substrate front side for the deposition of a first and second precursor material A and B, respectively, wherein the plurality of first gas distribution enclosures 150 and the plurality of second gas distribution enclosures 160 are arranged alternatingly.

[0061] In the section of the transportation path which transfers the flexible substrate 110 from processing drum 240 to processing drum 240', a further plurality of first gas distribution enclosures and a further plurality of second gas distribution enclosures can be arranged opposite to the substrate front side for the deposition of a first and second precursor material A and B, respectively, wherein the further plurality of first gas distribution enclosures and the further plurality of second gas distribution enclosures are arranged alternatingly. In this section of the transportation path, the flexible substrate can be transported in free-span manner supported by several guiding rollers 300.

[0062] The processing drum can be provided with a tempering unit configured for tempering the flexible substrate. Further, for tempering the substrate in the free-span section of the transportation path, the flexible substrate can be heated by heating units provided in the rear side of the flexible substrate. For sake of clarity, the tempering units are not shown in FIG. 7.

[0063] The embodiment according to FIG. 7 which can be combined with other embodiments described herein provides the possibility to increase the number of the plurality of first and second gas distribution enclosures. By increasing the number of the first and second gas distribution enclosures, an increased number of atomic layers of the barrier layer deposited by ALD can be deposited in a single processing cycle. This results in an increased thickness of the ALD barrier layer and/or an increased throughput, e.g. an increased

substrate transportation speed. An increased layer thickness of the ALD barrier layer stack can provide a decreased WVTR.

[0064] Between at least one first gas distribution enclosure 150 of the plurality of first gas distribution enclosures and at least one second gas distribution enclosure 160 of the plurality of second gas distribution enclosures, a gas separation stage can be arranged. In FIG.7, the gas separation stages are omitted for sake of clarity. A contact of the front side of the flexible substrate 110 with any roller can be avoided to keep the deposited layers free of defects.

[0065] According to embodiments which can be combined with other embodiments described herein, the roll-to-roll processing apparatus 225 as shown in FIG. 7 can be provided with at least one further deposition chamber. For example, the at least one further deposition chamber can be configured for plasma-enhanced chemical vapor deposition (PECVD). The at least one deposition chamber configured for plasma-enhanced chemical vapor deposition (PECVD) can be the first deposition chamber in the direction of transport of the flexible substrate downstream of the plurality of first gas distribution enclosures and the plurality of second gas distribution enclosures. The PECVD deposition chamber 260 can be configured to deposit a PECVD layer onto the barrier layer or barrier layer stack deposited by ALD. For example, the PECVD layer can be a SiO_2 layer, a SiNx layer, or a SiN layer.

[0066] Additionally or alternatively, a deposition chamber configured for plasma-enhanced chemical vapor deposition (PECVD) can be the first deposition chamber in the direction of transport of the flexible substrate downstream of the unwinding roller 230. The additional or alternative PECVD deposition chamber 260' configured for plasma-enhanced chemical vapor deposition (PECVD) provides the possibility to deposit a planarization layer deposited directly on the flexible substrate. The planarization layer can eliminate the unevenness or roughness of the surface of the flexible substrate. Surface roughness can lead to growth of nodules. Nodules in the barrier layer can be a reason for defects in the ALD barrier layer. By smoothing the substrate's surface, the planarization layer can further reduce the number of defects in the ALD barrier layer. The planarization layer can further reduce the WVTR of the barrier film.

[0067] Besides quantum dot enhancement films (QDEF), there are quantum dot LEDs (QD-LED) available. The structure of a QD-LED can include cadmium selenide (CdSe) nanocrystals as light emitting centers. The layer of cadmium-selenium quantum dots is sandwiched between layers of electron-transporting and hole-transporting organic materials. This layer stack can be sandwiched between a cathode layer and an anode layer, respectively. The organic materials of a QD display as well as the organic materials of an OLED display can be encapsulated by a barrier layer stack for reducing a degradation of the organic materials.

[0068] According to embodiments as described herein, an encapsulation of quantum dot structures can have the architecture: substrate/barrier layer stack/QDs/barrier layer stack/substrate as illustrated in FIG. 8. The substrate can be PET or a different flexible substrate. The barrier layer stack can include the ALD barrier layer and the PECVD barrier layer. A quantum dot structure can be a quantum dot enhancement film QDEF or a QD-LED structure.

[0069] The quantum dot encapsulation 310 can include a first barrier structure 100 and a second barrier structure 100'. The first barrier structure 100 can include a flexible substrate 110, a barrier layer 120 deposited by ALD, and a PECVD layer 130. On this barrier structure 100, a quantum dot structure 320 can be deposited directly. For encapsulation, a second barrier structure 100' can be laminated. The second barrier structure 100' can include a flexible substrate 110', a barrier layer 120' deposited by ALD, and a PECVD layer 130'. The PECVD layer 130' of the second barrier structure faces the quantum dot structure 320.

[0070] According to another embodiment as illustrated in FIG. 9, a quantum dot structure 320 can be deposited on a substrate 115. Substrate 115 can be made of a material having a WVTR lower than that of the barrier structure 100 and/or the barrier structure 100'. For example, substrate 115 can be a wafer, or a thin, bendable glass foil or a metal foil. For encapsulation, the quantum dot structure 320 can be covered with a barrier structure 100 which is arranged above the quantum dot structure 320.

[0071] FIG. 10 shows a flow chart illustrating a method 700 for depositing a barrier film on a flexible substrate according to embodiments described herein. According to an aspect of the present disclosure, the method 700 includes in block 710 continuously transporting a flexible substrate from an unwinding roller to a re-winding roller. According

to embodiments described herein, the method 700 further includes in block 720 contacting the flexible substrate on the back side thereof. According to embodiments described herein, the method 700 further includes in block 730 depositing a first precursor material on the flexible substrate in a first gas distribution enclosure arranged opposite to the substrate front side. According to embodiments described herein, the method 700 further includes in block 740 depositing a second precursor material on the flexible substrate in a second gas distribution enclosure arranged opposite to the substrate front side. According to embodiments described herein, the method 700 further includes in block 750 forming a product compound by a chemical reaction of the first precursor material and the second precursor material. According to embodiments described herein, the method 700 further includes in block 760 generating a barrier layer stack by repeating the deposition of the first precursor material and the second precursor material on the flexible substrate. According to embodiments described herein, the method 700 further includes in block 770 depositing a layer by plasma-enhanced chemical vapor deposition over the barrier layer stack.

[0072] FIG. 11 shows a flow chart illustrating a method 800 for encapsulating a quantum dot structure according to embodiments described herein. According to an aspect of the present disclosure, the method 800 includes in block 810 continuously transporting a flexible substrate. According to some embodiments, the method 800 further includes in block 820 depositing a first precursor material on the flexible substrate in a first gas distribution enclosure arranged opposite to the substrate front side. According to embodiments described herein, the method 800 further includes in block 830 depositing a second precursor material on the flexible substrate in a second gas distribution enclosure arranged opposite to the substrate front side. According to embodiments described herein, the method 800 further includes in block 840 forming a product compound by a chemical reaction of the first precursor material and the second precursor material. According to embodiments described herein, the method 800 further includes in block 850 generating a barrier layer stack by repeating the deposition of the first precursor material and the second precursor material on the flexible substrate. According to embodiments described herein, the method 800 further includes in block 860 depositing a layer by plasma-enhanced chemical vapor deposition over the barrier layer stack to form a quantum dot encapsulation for encapsulating one or more quantum dot structures with at least one first encapsulation layer stack. According to further embodiments described herein, the method 800 includes forming

at least one second encapsulation layer stack and encapsulating the one or more quantum dot structures between at least two encapsulation layer stacks.

[0073] The present disclosure has several advantages including a continuously deposited ALD layer on flexible substrates particularly on elongated flexible substrates such as foils bands or tapes, avoiding a front contact of the flexible substrate by the transport rollers, providing a PECVD barrier layer on the ALD layer without breaking the vacuum of the processing apparatus, and/or producing a barrier layer of improved barrier effect.

[0074] While the foregoing is directed to embodiments of the disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

CLAIMS

1. A processing apparatus for atomic layer deposition of a thin film on a flexible substrate, comprising:

a substrate support configured to continuously transport the flexible substrate;

a plurality of first gas distribution enclosures arranged opposite to a substrate front side for providing a first precursor material on the front side of the flexible substrate; and

a plurality of second gas distribution enclosures arranged opposite to the substrate front side for providing a second precursor material on the front side of the flexible substrate, wherein the plurality of first gas distribution enclosures and the plurality of second gas distribution enclosures are arranged alternatingly.

2. The processing apparatus according to claim 1, wherein the substrate support configured to continuously transport the flexible substrate from a first position to a second position different than the first position, and wherein the plurality of alternatingly arranged first and second gas distribution enclosures are arranged in series between the first position and the second position.

3. The processing apparatus according to any of claims 1 or 2, further comprising:

at least one gas separation stage arranged between at least one first gas distribution enclosure of the plurality of first gas distribution enclosures and at least one second gas distribution enclosure of the plurality of second gas distribution enclosures.

4. The processing apparatus according to any of claims 1 or 2, further comprising:

an excitation unit configured to induce a chemical reaction, particularly wherein the excitation unit is provided in the at least one of a first or second gas distribution enclosure.

5. The processing apparatus according to claim 3, wherein the excitation unit is a plasma source or a heater.

6. The processing apparatus according to any of the preceding claims, further comprising at least one deposition chamber configured for plasma-enhanced chemical vapor deposition (PECVD).

7. The processing apparatus according to claim 5, wherein the at least one deposition chamber configured for plasma-enhanced chemical vapor deposition (PECVD) is a first deposition chamber in a direction of transport of the flexible substrate downstream of the plurality of first gas distribution enclosures and the plurality of second gas distribution enclosures.

8. The processing apparatus according to any of the preceding claims, wherein the plurality of first gas distribution enclosures and/or the plurality of second gas distribution enclosures comprise a gas distribution plate.

9. The processing apparatus according to any of the preceding claims, wherein the plurality of first gas distribution enclosures and/or the plurality of second gas distribution enclosures comprise a gas lance with openings.

10. The processing apparatus according to any of the preceding claims, further comprising:

a winding system for transporting said flexible substrate from an unwinding roller to a re-winding roller, wherein the substrate support is at least one processing drum configured to continuously transport the flexible substrate and to contact the flexible substrate on a back side thereof.

11. A barrier layer stack deposited onto a flexible substrate, the barrier layer stack comprising at least one barrier layer deposited by atomic layer deposition followed by at least one barrier layer deposited by plasma-enhanced chemical vapor deposition having an overall thickness of at least 100 nm.

12. The barrier layer stack according to claim 11, wherein a material of the at least one barrier layer is selected from the group consisting of Al_2O_3, TiO_2, ZrO_2, SiO_2, HfO_x, and combinations thereof .

13. A roll-to-roll processing apparatus for atomic layer deposition of a thin film on a flexible substrate, comprising:

a winding system for transporting said flexible substrate from an unwinding roller to a re-winding roller;

a substrate support configured to continuously transport the flexible substrate and to contact the flexible substrate on a back side thereof;

a plurality of first gas distribution enclosures arranged opposite to a substrate front side for deposition of a first precursor material;

a plurality of second gas distribution enclosures arranged opposite to the substrate front side for deposition of a second precursor material, wherein the plurality of first gas distribution enclosures and the plurality of second gas distribution enclosures are arranged alternatingly;

at least one gas separation stage arranged between at least one first gas distribution enclosure of the plurality of first gas distribution enclosures and at least one second gas distribution enclosure of the plurality of second gas distribution enclosures; and

an excitation unit coupled to the at least one first or second gas distribution enclosure configured to induce a chemical reaction, wherein the excitation unit is a plasma source.

14. A method for depositing a barrier film on a flexible substrate comprising:

continuously transporting a flexible substrate from an unwinding roller to a re-winding roller;

contacting the flexible substrate on a back side thereof;

depositing a first precursor material on the flexible substrate in a first gas distribution enclosure arranged opposite to a substrate front side;

depositing a second precursor material on the flexible substrate in a second gas distribution enclosure arranged opposite to the substrate front side;

forming a product compound by a chemical reaction of the first precursor material and the second precursor material;

generating a barrier layer stack by repeating the deposition of the first precursor material and the second precursor material on the flexible substrate; and

depositing a layer by plasma-enhanced chemical vapor deposition over the barrier layer stack.

15. A method for encapsulating a quantum dot structure, comprising:

continuously transporting a flexible substrate;

depositing a first precursor material on the flexible substrate in a first gas distribution enclosure arranged opposite to a substrate front side;

depositing a second precursor material on the flexible substrate in a second gas distribution enclosure arranged opposite to the substrate front side;

forming a product compound by a chemical reaction of the first precursor material and the second precursor material;

generating a barrier layer stack by repeating the deposition of the first precursor material and the second precursor material on the flexible substrate;

depositing a layer by plasma-enhanced chemical vapor deposition over the barrier layer stack to form a quantum dot encapsulation layer stack; and

encapsulating one or more quantum dot structures with the quantum dot encapsulation layer stack.

16. The method according to claim 15, further comprising:

forming at least one second quantum dot encapsulation layer stack and encapsulating the one or more quantum dot structures between the quantum dot encapsulation layer stack and at least one second encapsulation layer stack.

Fig. 1

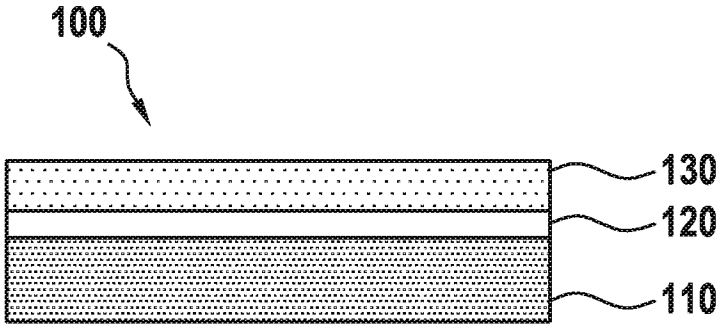

100
130
120
110

Fig. 2

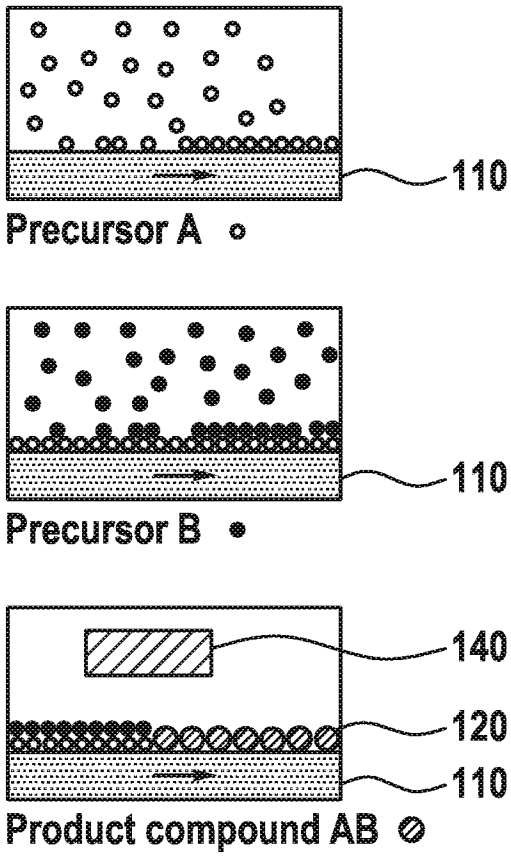

110
Precursor A
110
Precursor B
140
120
110
Product compound AB

Fig. 3a

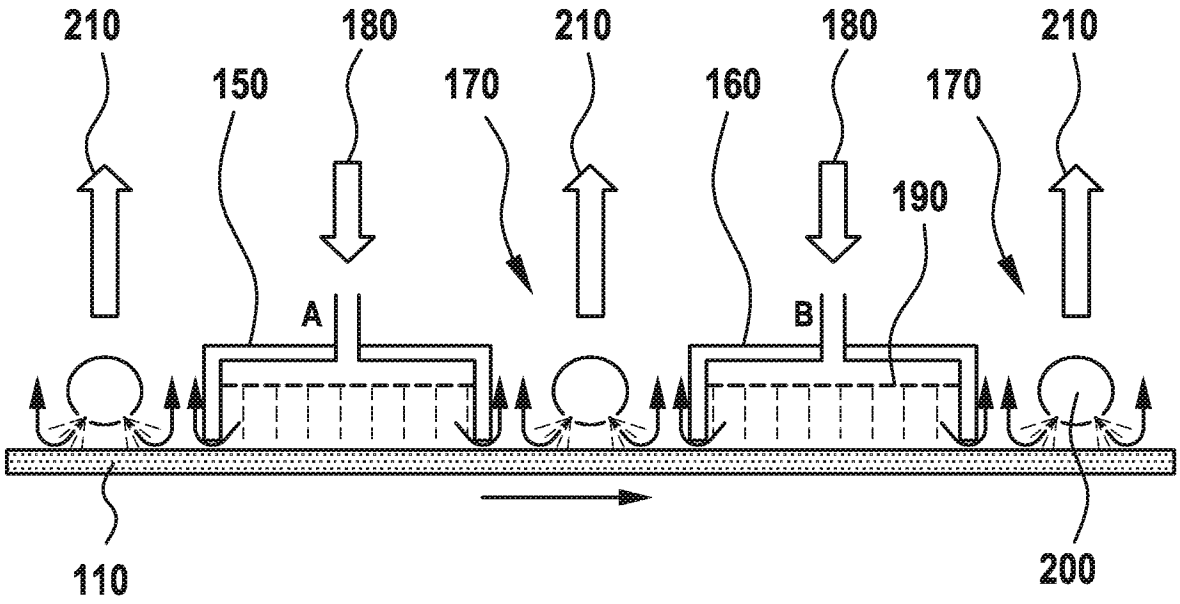

210
180
210
180
210
150
170
160
170
190
A
B
110
200

Fig. 3b

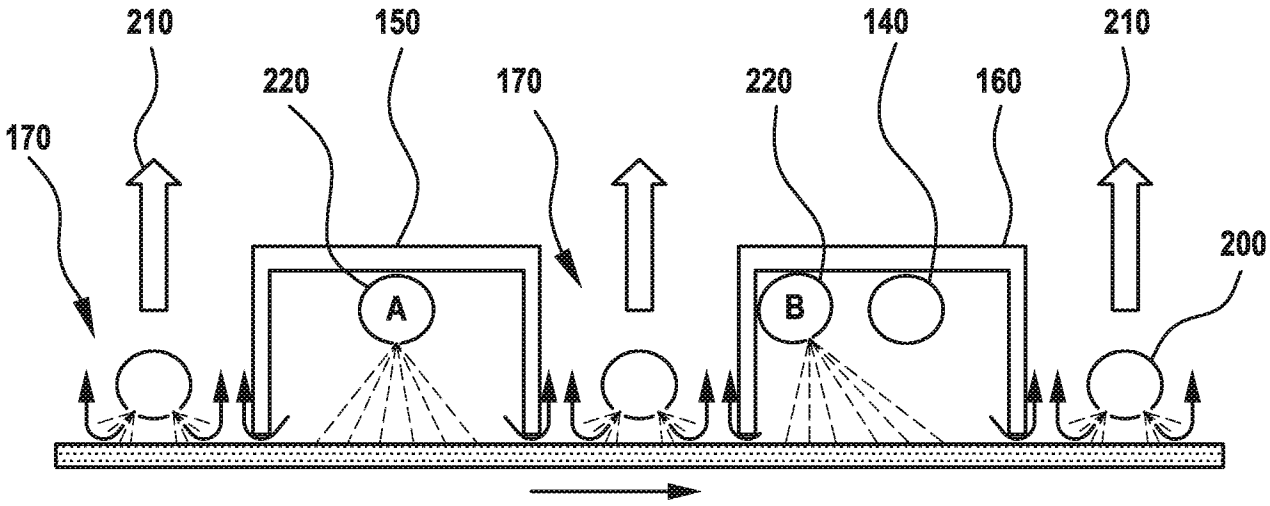

210
150
140
210
220
170
220
160
170
200
A
B

Fig. 4

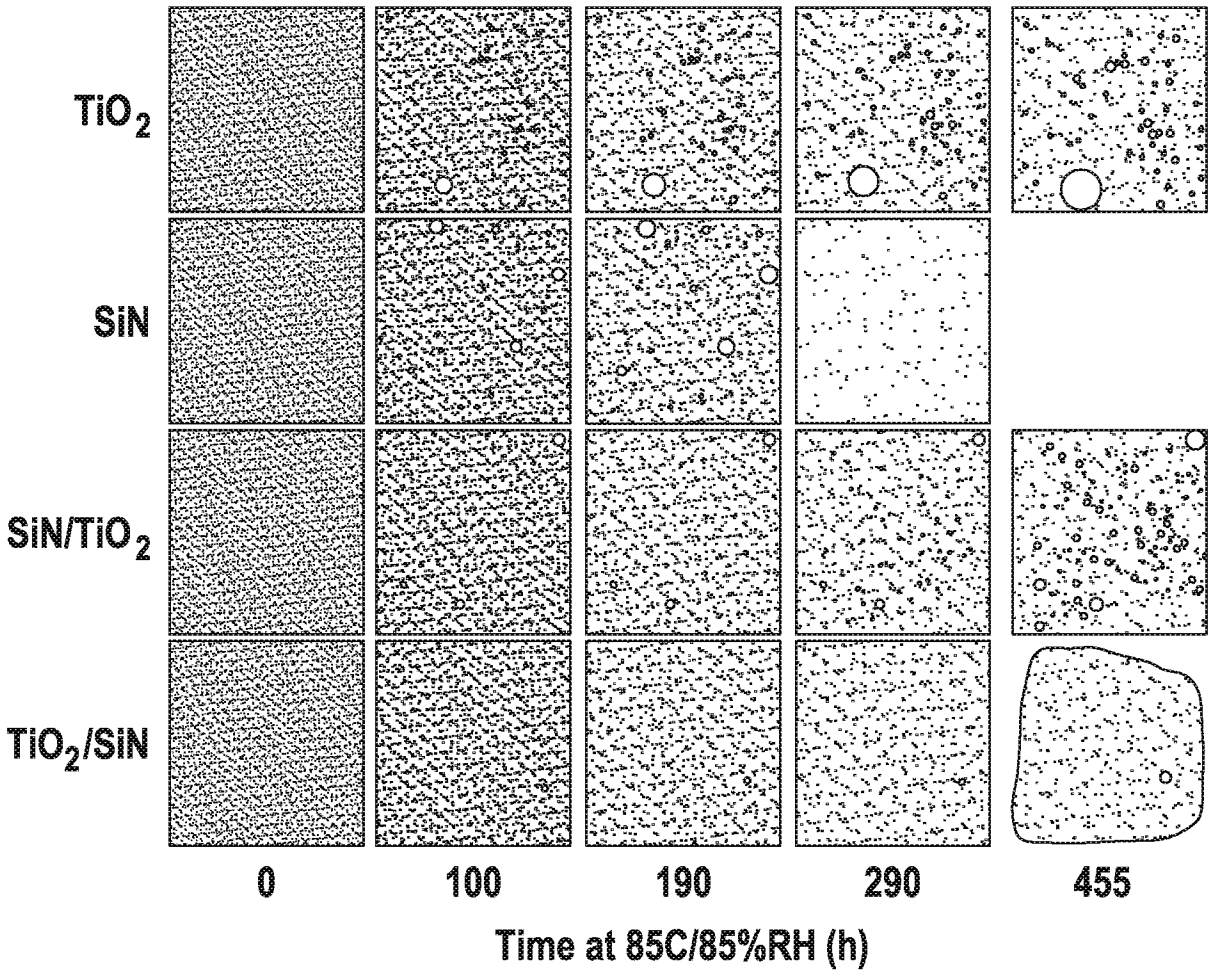


Fig. 5a

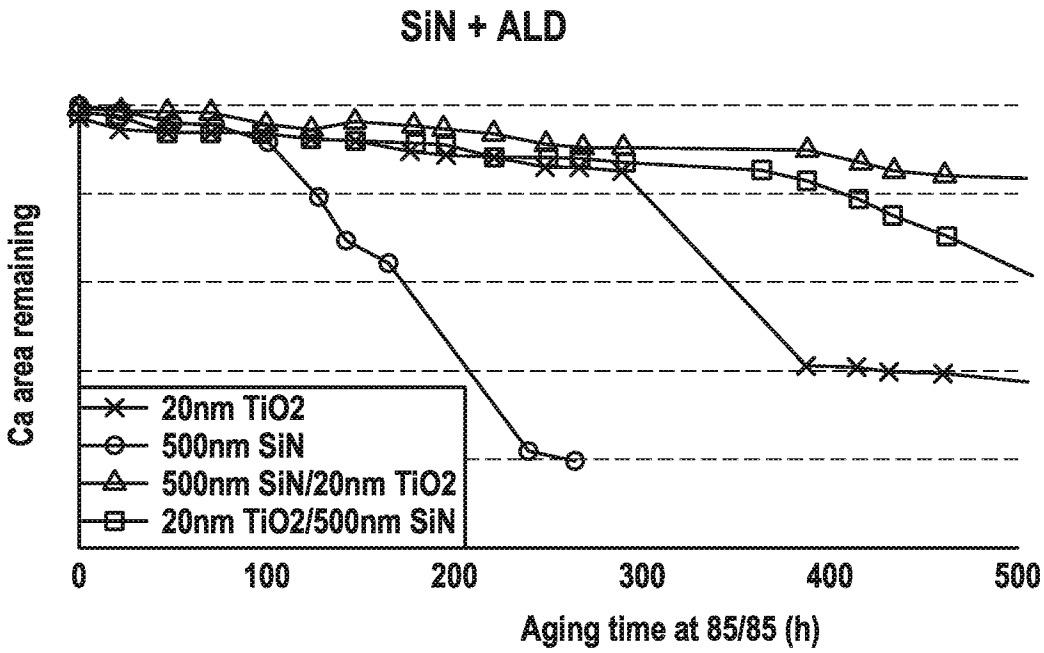

SiN + ALD
Ca area remaining
20nm TiO2
500nm SiN
500nm SiN/20nm TiO2
20nm TiO2/500nm SiN
0
100
200
300
400
500
Aging time at 85/85 (h)

Fig. 5b

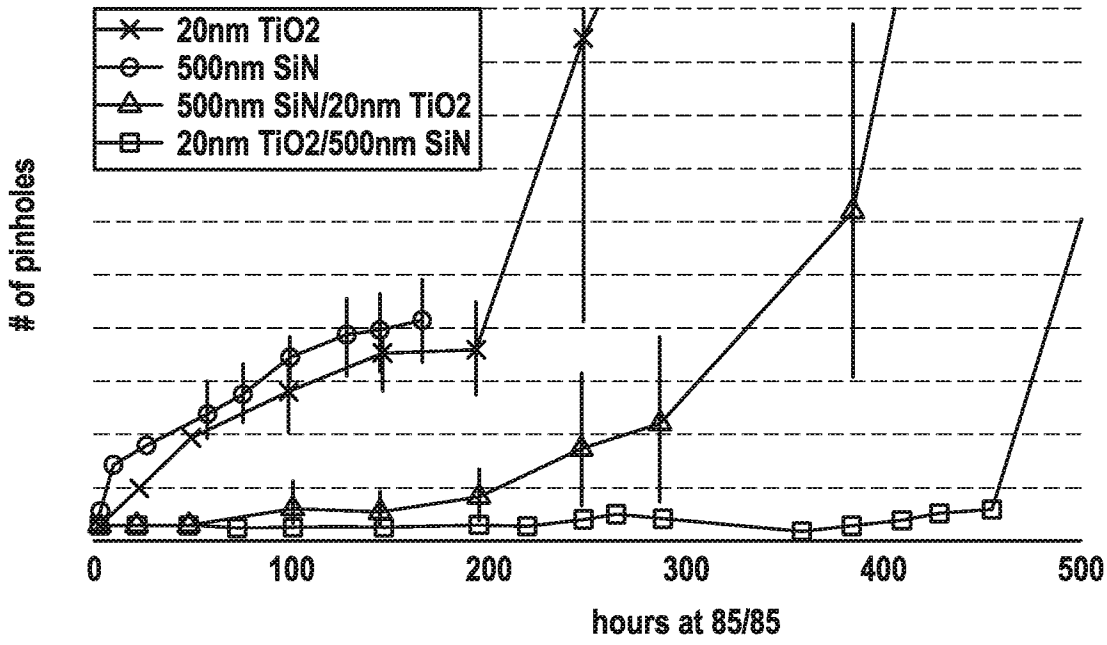
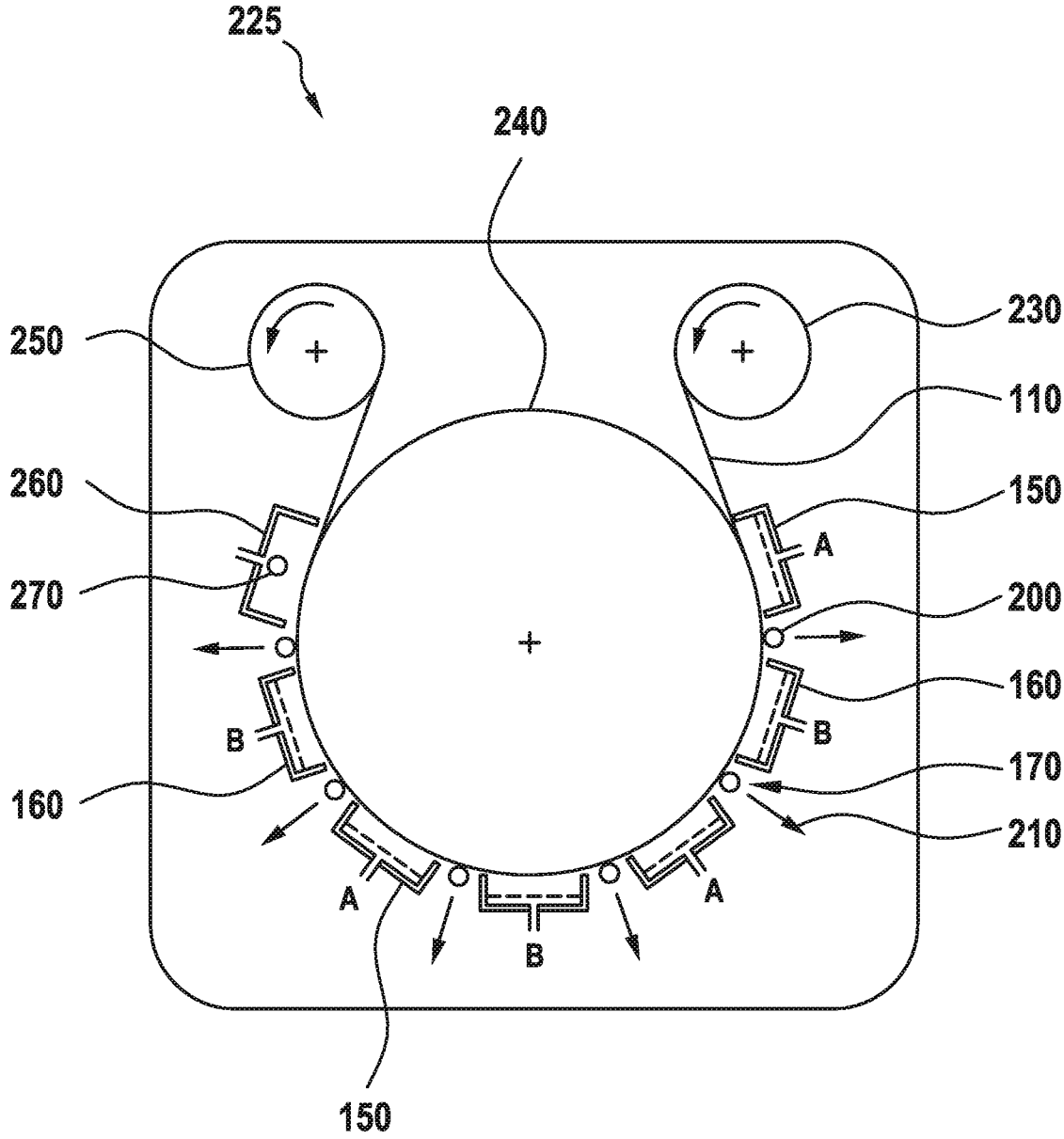

20nm TiO2
500nm SiN
500nm SiN/20nm TiO2
20nm TiO2/500nm SiN
# of pinholes
0
100
200
300
400
500
hours at 85/85

Fig. 6



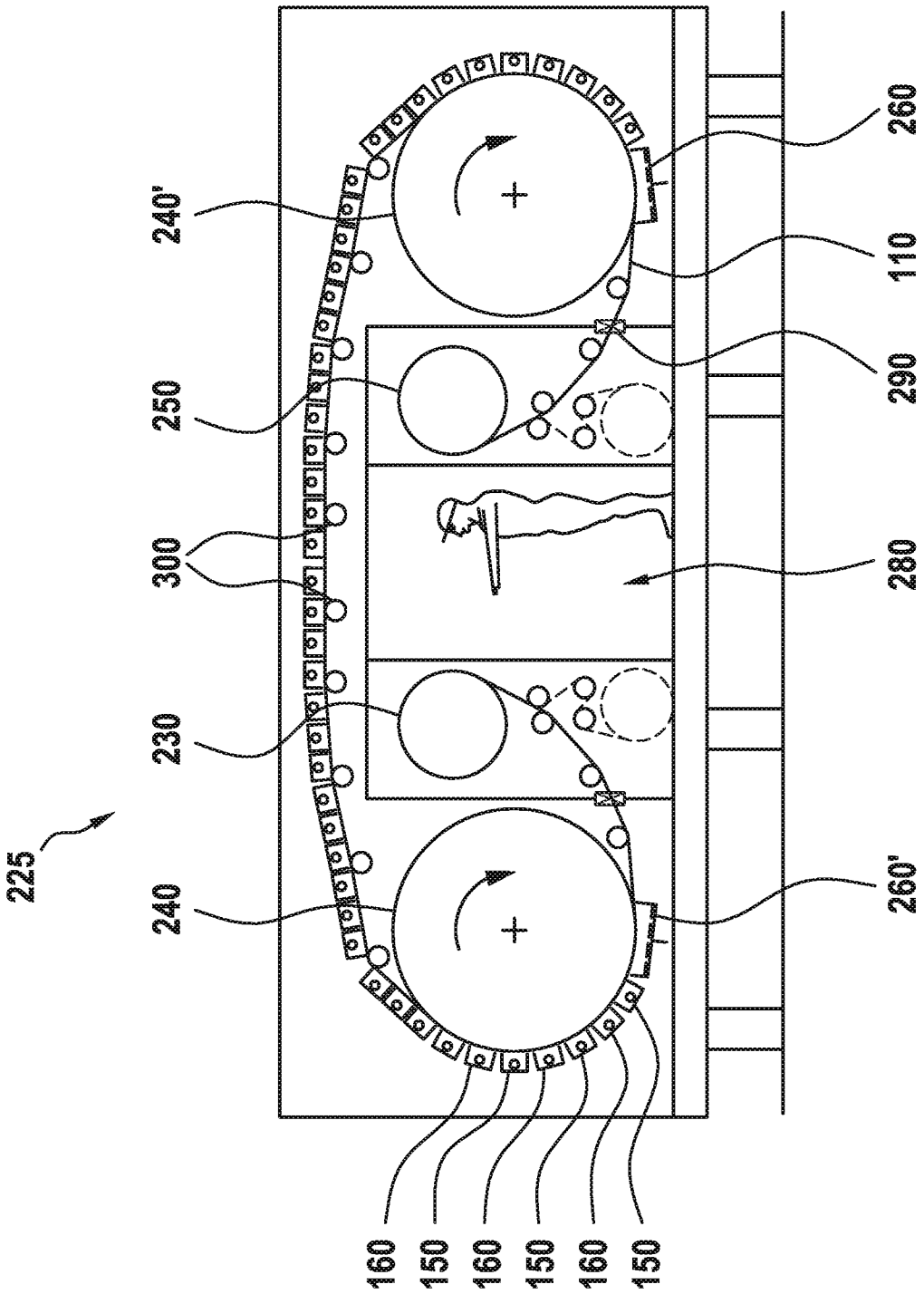

225
240
230
300
250
240'
260'
280
290
110
260
160
150
160
150
160
150

Fig. 7

Fig. 8

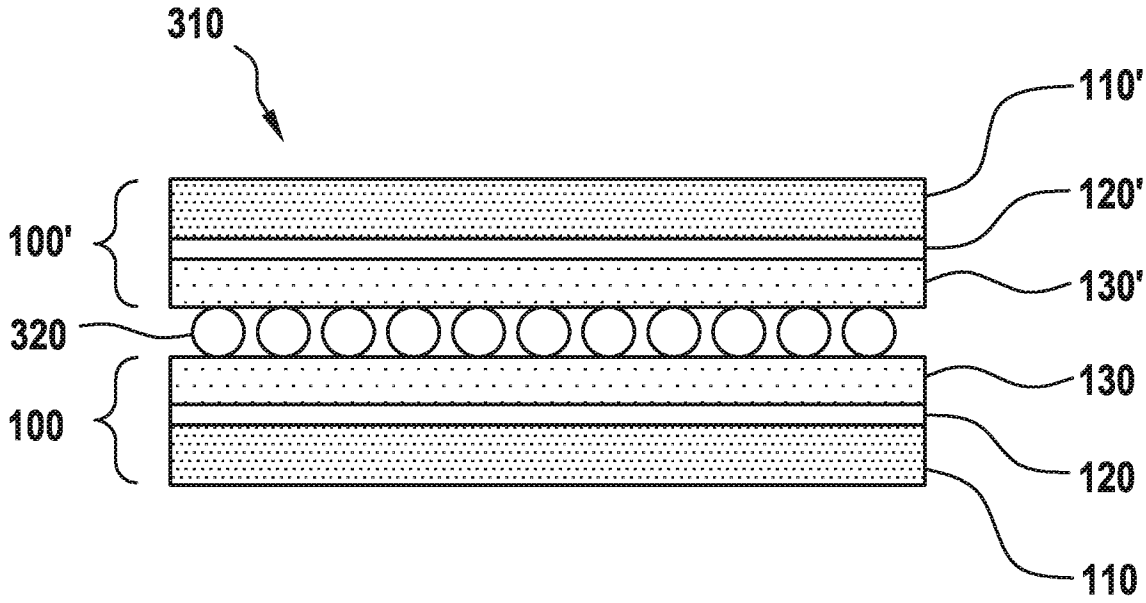

310
110'
120'
130'
100'
320
130
100
120
110

Fig. 9

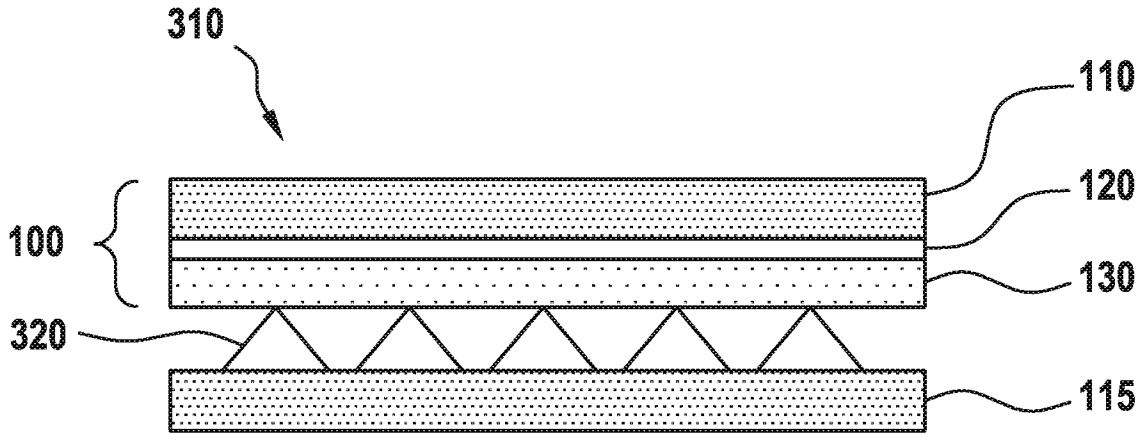

310
110
120
130
100
320
115

Fig. 10

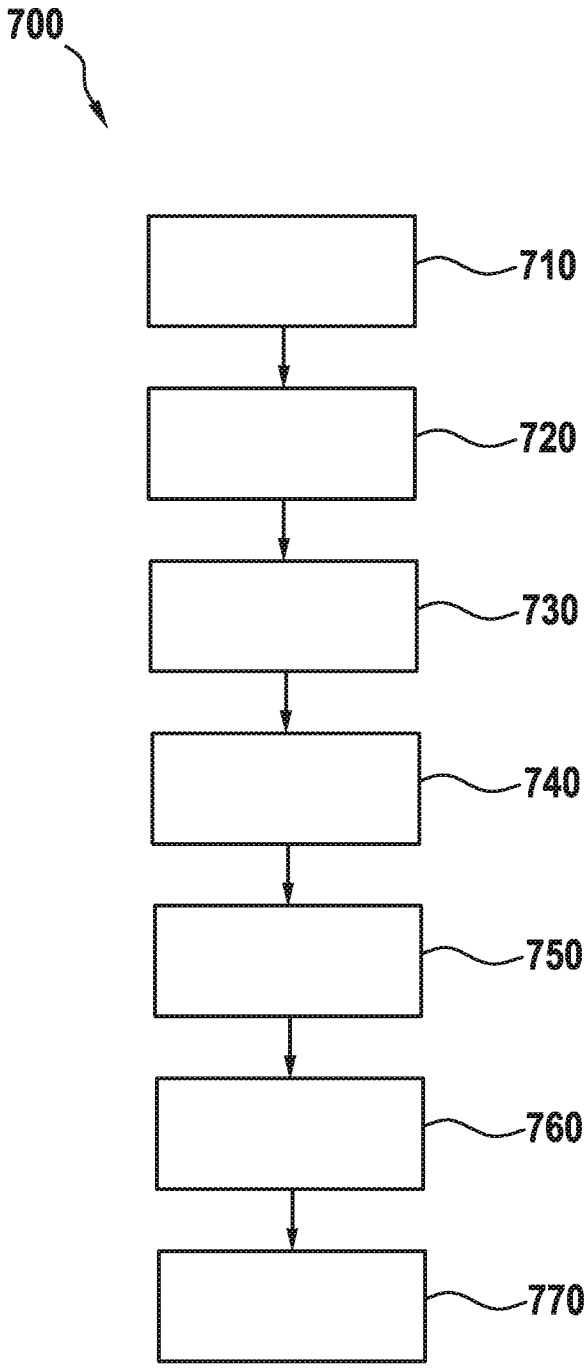
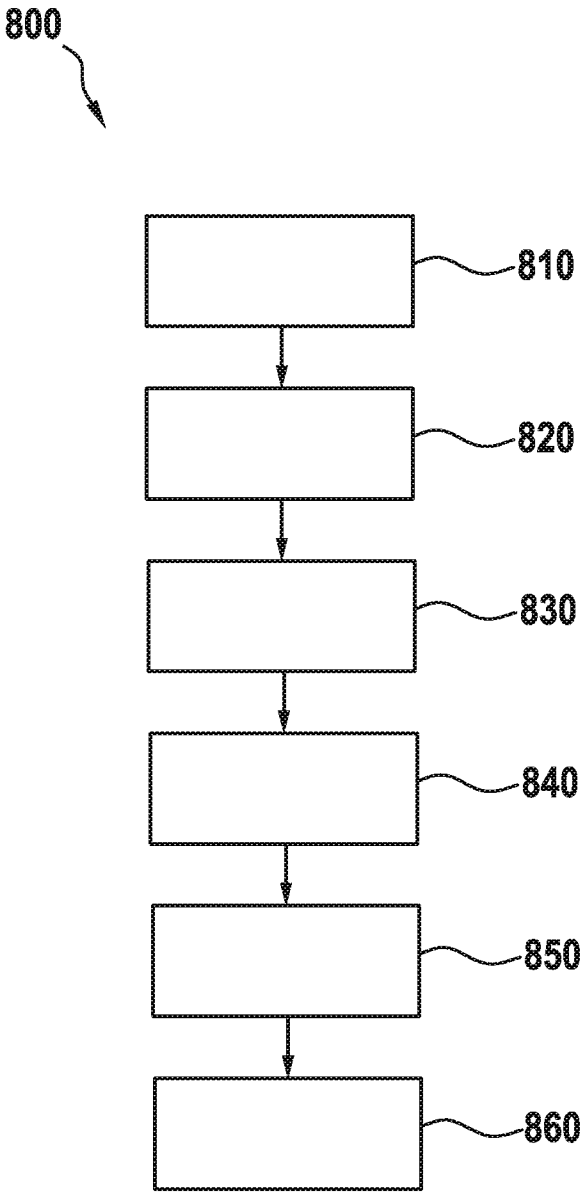


Fig. 11



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/029621

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/50 C23C16/455 C23C16/54 C23C16/34 C23C16/40
H01L51/50 H01L33/50
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 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.
X	US 2015/247241 A1 (EZURE HIDETOSHI [JP]) 3 September 2015 (2015-09-03) paragraphs [0128], [0131]	11,12
X	US 2007/224348 A1 (DICKEY ERIC R [US] ET AL) 27 September 2007 (2007-09-27)	1-7,10, 13
Y	paragraph [0040]; figure 3 paragraph [0051]	8,9
Y	US 2011/097494 A1 (KERR ROGER S [US] ET AL) 28 April 2011 (2011-04-28) paragraph [0108]; figure 28a	8
Y	US 2010/229797 A1 (KATO HITOSHI [JP] ET AL) 16 September 2010 (2010-09-16) paragraph [0040]; figure 2	9

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"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	Date of mailing of the international search report
25 January 2017	02/02/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kudelka, Stephan

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/029621

C(Continuation). 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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Y	paragraph [0281] paragraph [0301]; figure 8 paragraph [0307]	15,16
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