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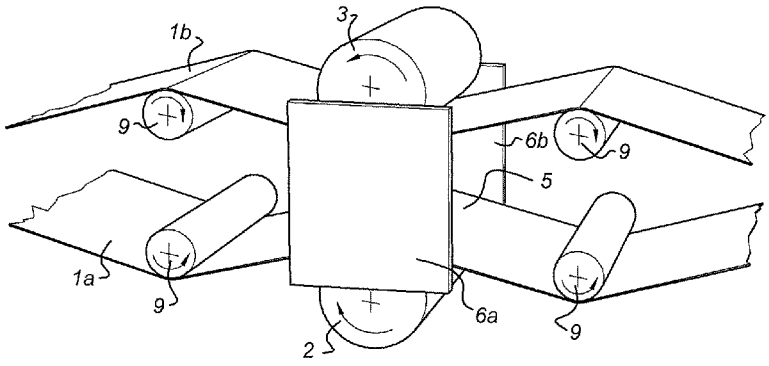
(54) **Title**: METHOD AND DEVICE FOR MANUFACTURING A BARRIER LAYER ON A FLEXIBLE SUBSTRATE

Fig 1c



(57) **Abstract**: The invention provides a method for manufacturing a barrier layer on a substrate, the method comprising: - providing a substrate with an inorganic oxide layer having a pore volume between 0.3 and 10 vol. %; - treating said substrate with an inorganic oxide layer in a glow discharge plasma, said plasma being generated by at least two electrodes in a treatment space formed between said two electrodes, said treatment space also being provided with a gas comprising Nitrogen compounds; and - the treating of the substrate in said treatment space is done at a temperature below 150°C, e.g. below 100°C. The invention further provides a device for manufacturing a barrier layer on a substrate.

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METHOD AND DEVICE FOR MANUFACTURING A BARRIER LAYER ON A FLEXIBLE SUBSTRATE

TECHNICAL FIELD

The invention relates to a method for manufacturing a barrier layer on a substrate. The present invention further relates to a device for manufacturing such a barrier layer. In addition the invention relates to a substrate having an inorganic oxide barrier layer.

BACKGROUND

Nitridation techniques using a nitrogen plasma have been widely studied for application to integrated electronics devices such as gate insulators of metal oxide semiconductor field effect transistors.

For example US 7 619 356 describes an anode for an OLED device wherein the anode comprises an Indium Tin Oxide (ITO) film on a glass substrate and the ITO surface is being treated in a plasma treatment at low pressure (14 mTorr) at 50 W power for 5 minutes. As a result of this treatment 13.3% nitrogen atoms are observed from the surface, which amount corresponds to about 275 oxygen atoms.

US 7 132 373 discloses a method for producing a crystalline metal oxide film (for example a film containing ITO) using a nitrogen or oxygen plasma at a low pressure (50-100 Pa) for at least 3 minutes.

US 7 898 082 discloses a semiconductor device having a barrier metal nitride layer, the layer formed using a nitrogen plasma at high temperatures of 350-750 degrees Celsius.

Furthermore, Nakae et al describes in the Journal of Applied Physics 101, 023513 (2007) the grow models of silicon nitride ultrathin films fabricated using atmospheric pressure plasma on Si-wafers. In case of nitridation with an RF plasma this was done at a low gas pressure of $1.0 * 10^{-5}$ Torr.

JP 4 249 520 discloses the improvement of using a nitridation step with an Argon and Nitrogen plasma treatment at low pressure.

In many manufacturing processes involving glass substrates, such as the process of manufacturing OLED devices, there is a desire to replace glass substrates with low

weight, flexible polymeric substrates using polymers with a very thin amorphous layer of metal oxide with improved barrier properties.

It is an object of the invention to provide a method for creating an improved barrier on a substrate, in particular a flexible substrate.

SUMMARY OF THE INVENTION

According to a present invention embodiment, a method is provided for manufacturing a barrier layer on a substrate, the method comprising:

- providing a substrate with an inorganic oxide layer having a pore volume between 0.3 and 10 vol. % ;

- treating said substrate with an inorganic oxide layer in a glow discharge plasma, said plasma being generated by at least two electrodes in a treatment space formed between said two electrodes, said treatment space also being provided with a gas comprising Nitrogen compounds; and

- the treating of the substrate in said treatment space is done at a temperature below 150^0C, e.g. below 100^0C.

In an embodiment, the treatment is done until a barrier with a top layer comprising between 1 to 3% Nitrogen-atom concentration is formed on the substrate.

In an embodiment the generated plasma is a high frequency or radio frequency (RF) plasma or discharge.

In an embodiment, the gas comprising Nitrogen compounds comprises N_2 (nitrogen) and/or NH_3 (ammonia) and/or NO.

In an embodiment, the gas comprising Nitrogen compounds has a pressure between 0.1 and 10 atmosphere, e.g. between 0.5 and 5 atmosphere (between $5x10^4$ Pa and $5x10^5$ Pa), e.g. between 0.6 and 2 atmosphere (between $6x10^4$ Pa and $2x10^5$ Pa), e.g. substantially 1 atmosphere. At these pressures, typically higher than used in the prior art, the barrier is advantageously formed in less time.

In an embodiment, the treating of the substrate in said treatment space is done for a duration of less than 20 minutes, e.g. less than 10 minutes. Given the conditions outlined above, this is enough time to form a suitable barrier layer, in particular a barrier having a top layer with 1 to 3% Nitrogen atom concentration.

In an embodiment, the substrate is a flexible substrate, in particular a flexible polymeric substrate. In a further embodiment, the electrodes are roll-electrodes, and the flexible layer is moved through the treatment space at a linear speed.

In an embodiment, the inorganic oxide layer of the provided substrate is an silicon-oxide layer.

In an embodiment, the top layer of the barrier that is formed is between 5 and 15 nm, e.g. between 7 and 12 nm, thick.

The invention further provides a device for manufacturing a barrier layer on a substrate, the device comprising:

- at least two electrodes, arranged to generate a glow discharge plasma in a treatment space formed between said two electrodes;

- a gas supply device, arranged to provide a gas comprising Nitrogen compounds to the treatment space;

- wherein the treatment space if further arranged to hold and treat at least one substrate having an inorganic oxide layer, and the device is arranged for treating of the substrate in said treatment space at a temperature below 150^0C, e.g. below 100^0C. The device can further have any of the previously mentioned features of embodiments of the invention.

The invention further provides a substrate having a barrier layer, the barrier layer comprising an inorganic oxide layer originally, that is, prior to a nitridation step, having a pore size between 0.3 and 10 vol. %, the inorganic oxide layer further having a top layer comprising between 1 to 3% Nitrogen-atom concentration. The substrate and/or the barrier layer may further have any of the abovementioned substrate and/or barrier layer features.

The method and device described in this invention gives a remarkable improvement, which is not known from the prior art, using a nitridation step at atmospheric pressure and relatively low temperatures resulting in a product having a small amount concentration N-atoms built-in in the metal oxide surface. The method and device according the invention thus allows the manufacturing of an excellent barrier film, wherein said film may essentially consist of a flexible substrate having a thin inorganic oxide layer having a pore volume from e.g. 0.1 to 20 volume %, e.g. 0.3

to 10 volume %. The method can yield a sealed inorganic oxide layer having between 1 and 3% nitrogen atom concentration in the first 10 nm top layer of the inorganic film. The method comprises at least a treatment step wherein said substrate with the inorganic oxide layer is treated in a plasma, such as an atmospheric plasma, more in particular an atmospheric pressure glow discharge plasma that is generated in a treatment space formed between at least two electrodes, by applying an electrical power from a power supply to the at least two electrodes, resulting in the treatment space in a high frequency electromagnetic field. Said treatment step e.g. lasts for less than 10 minutes at a temperature below 150^0C, during which the treatment space being filled with a gas composition comprising a nitrogen compound such as N_2 (nitrogen) or NH_3 (ammonia) or NO or a combination thereof.

In another embodiment besides the above mentioned Nitrogen-based molecules, the gas composition may in addition contain a small amount of H_2 (hydrogen) gas, which may influence the plasma and barrier properties advantageously.

As a result of the treatment the inorganic oxide layer becomes sealed and gains a barrier improvement of a factor 1000, which was an unforeseen and surprising effect.

The method is preferably practiced on a flexible substrate with an inorganic oxide layer having a pore size of 0.1 to 20 volume %, e.g. 0.3 to 10 volume %. A variety of methods are possible for the provision of said substrate, which may be a sputtering method, an ion plating method, and a vacuum evaporation method. Alternatively, the inorganic oxide film can be formed by application of a precursor solution, that is, a wet deposition. In the latter case, the above-mentioned inorganic oxide layer may also be pretreated by ultraviolet light irradiation prior to exposing to plasma.

The inorganic oxide film substantially is, for example, a thin layer containing a silicon oxide, titanium oxide, aluminum oxide, film containing ITO and the like. The inorganic oxide film thickness may vary between 10 and 1000 nm. Examplary ranges may be between 15 and 100 nm.

In an embodiment the inorganic oxide film is prepared by exposing a flexible polymeric substrate to an atmospheric plasma deposition apparatus using a precursor as disclosed in EP 1 917 842 by applicant and which is hereby incorporated as reference. Preferred precursors which may be used for forming an inorganic oxide layer on a

flexible substrate by using an atmospheric plasma as described in WO 2009 104 957 are TEOS, HMDSO, TPOT, TEOT, TMA, TEA.

The flexible substrate may be any kind of polymeric film. In an exemplary embodiment PET or PEN film is used having a thickness of 50 to 200 μm.

Other examples of substrate which may be used are transparent sheets of ethylene vinyl acetate (EVA), of polyvinyl butyral (PVB), of polytetrafluoroethylene (PTFE), perfluoroalcoxy resins (PFA), i.e., copolymers of tetrafluoroethylene and perfluoroalkyl vinyl ether, tetafluoroethylene-hexafluoropropylene copolymers (FEP), tetrafluoroethylene-perfluoroalkyl vinyl ether-hexafluoro-propylene copolymers (EPE), tetrafluoroethylene-ethylene or propylenecopolymers (ETFE), polychlorotrifluoroethylene resins (PCTFE), ethylene-chlorotrifluoroethylene copolymers (ECTFE), vinylidene fluoride resins (PVDF), and polyvinyl fluorides (PVF) or coextruded sheets from polyester with EVA, polycarbonate, polyolefin, polyurethane, liquid crystal polymer, aclar, aluminum, of sputtered aluminum oxide polyester, sputtered silicon oxide or silicon nitride polyester, sputtered aluminum oxide polycarbonate, and sputtered silicon oxide or silicon nitride polycarbonate.

SHORT DESCRIPTION OF THE FIGURES

The present invention will be discussed in more detail below, using a number of exemplary embodiments, with reference to the attached drawings, in which

Figures 1a, 1b, and 1c show schematic views of a plasma generation device according the invention.

Figure 2 shows the Electron Spectroscopy for Chemical Analysis (ESCA) or X-ray Photoelectron Spectroscopy (XPS) result of the top surface of an embodiment after an atmospheric pressure glow discharge nitridation treatment.

Figure 3 shows the ESCA (XPS) result of the top surface of a corona N_2 treatment of example 1.

DETAILED DESCRIPTION OF THE EXAMPLES

The present invention will now be described in reference to exemplary embodiments of the invention.

Figure 1a shows a schematic view of a plasma apparatus with which the present invention may be practiced. A treatment space 5, which may be a treatment chamber within an enclosure (not shown in figure 1a), or a treatment space 5 with an open structure, comprises two electrodes 2, 3. In general the electrodes 2, 3 are provided with a dielectric barrier 2a, 3a (see figure 1b) in order to be able to generate and sustain a glow discharge at atmospheric pressure in the treatment space. In the embodiment shown, the electrodes 2, 3 are planar electrodes, and the treatment space 5 is a rectangular space. A side tab 6 is provided to close off the treatment space 5 on one side.

However, other forms of the electrodes 2, 3 and of the gap or treatment space 5 are possible, e.g. as part of a cylindrical arrangement of the plasma treatment apparatus. E.g., the treatment space may be cylindrical, or elliptic, or have another form adapted to treat a specific type of substrate 1. Both electrodes 2, 3 may have the same configuration being flat orientated (as shown in figure 1a) or both being roll-electrodes (as shown in figure 1c). Also different configurations may be applied using a roll electrode and a flat or cylinder segment shaped electrode opposing each other. In further embodiments, the electrodes may be multi-segment electrodes. Embodiments using more than two electrodes are also imaginable.

In general the atmospheric pressure plasma is generated between the two electrodes 2, 3 in the treatment space 5. Alternatively a plurality of electrodes 2, 3 is provided. In case the electrodes 2, 3 have a surface area which is at least as big as the substrate 1, the substrate 1 can be fixed in the treatment space 5 between the two electrodes 2, 3.

Figure 1b shows a variant wherein two substrates 1a, 1b are treated simultaneously. In this alternative embodiment, not one substrate 1 but two substrates (1a, 1b) are positioned in a fixed way or moving at a certain speed in the treatment space 5 to utilise the gas supply even more efficiently. In figure 1c a further example of such an embodiment comprising two side tabs 6a, 6b and two substrates 1a, 1b is shown.

Both electrodes 2, 3 can be provided with a dielectric barrier layer 2a, 3a (see figure 1b). The dielectric layer 2a on the first electrode 2 has a thickness of d1 (mm),

and the dielectric layer 3a on the second electrode 3 has a thickness of d2 (mm). In operation, the total dielectric distance d of the electrode configuration also includes the thickness of the (one or two) substrates 1a, 1b to be treated, indicated by f1 (mm) and f2 (mm). Thus, the total dielectric thickness of the dielectric barrier in the treatment space 5 between the at least two opposing electrodes (2, 3) equals d = d1+f1+f2+d2.

In a further embodiment, both d1 and d2 are 0 and the only dielectric material forming the dielectric barrier is the substrate 1a, 1b. In case of two substrates 1a and 1b, the total dielectric thickness in this case is d= f1 + f2.

In still another embodiment both d1 and d2 are 0 and only one substrate 1 is used. In this embodiment the total dielectric thickness equals f1, so d = f1. Also in this embodiment in which electrode 3 is not covered with a dielectric material it is possible to obtain a stable atmospheric glow discharge plasma. The gap distance g in figure 1c indicates the smallest gap between the electrodes 2, 3 where an atmospheric pressure glow discharge plasma can exist in operation (i.e. in the treatment space 5), also called the free inter-electrode space. The dimensions of the electrodes 2, 3, dielectric barrier layers 2a, 3a, and gap g between the electrodes 2, 3, are predetermined in order to generate and sustain a glow discharge plasma at atmospheric pressure in the treatment space 5.

The dimensions of the electrodes 2, 3, dielectric barrier layers 2a, 3a, and gap g between the electrodes 2, 3 and the total dielectric distance (d) which is the total dielectric thickness of the dielectric barrier are controlled in a further embodiment, such that the product of gap distance and the total dielectric distance is arranged to be less than or equal to 1.0 mm^2 or even more preferred less than 0.5 mm^2 as disclosed in WO 2009/104 957 by applicant and is hereby incorporated as reference.

In case the substrate 1 is larger than the electrode area, the substrate 1 may be moved through the treatment space 5, e. g. at a linear speed using a roll-to-roll configuration, an example of which is shown in the embodiment of figure 1c. The substrates 1a, 1b are guided in close contact with the roller shaped (roll) electrodes 2, 3, using guiding rollers 9. A roll-electrode is e.g. implemented as a cylinder shaped electrode, mounted to allow rotation in operation e.g. using a mounting shaft or bearings. Such a roll-electrode may be freely rotating, or may be driven at a certain

angular speed, e.g. using well known controller and drive units. The side tabs 6a, 6b are positioned at the roller end faces, thereby creating a closed off treatment space 5 between the electrodes 2, 3.

The electrodes 2, 3 are connected to a power supply 4, which is arranged to provide electrical power to the electrodes for generating the atmospheric (glow discharge) plasma.

The power supply can be a power supply providing a wide range of frequencies for example f = 10 kHz – 30MHz .

Very good results can be obtained by using an atmospheric pressure glow discharge (APGD) plasma. Until recently these plasma's suffered from a bad stability, but using the stabilization circuits as for example described in US 6 774 569, EP 1 383 359, EP 1 547 123 and EP 1 626 613 (which are incorporated herein by reference), very stable APG plasma's can be obtained. In general these plasma's are stabilized by a stabilization circuit 21 (as shown figure 1a) counteracting local instabilities in the plasma. Using the stabilization circuit 21 in combination with the AC power source 20 in the power supply 4 for the plasma generating apparatus results in a controlled and stable plasma, without streamers, filamentary discharges or other imperfections.

In the plasma treatment apparatus a gas supply device 8 may be arranged for the substrate treatment in order to direct the gas for the nitridation step towards an inner region of the substrate to be processed. The supply device 8 also acts as the main carrier gas supply. A carrier gas may be used such as Argon, Helium, etc., to form the plasma, as an additive or mixture to reduce the breakdown voltage.

A gas supply inlet 8a may be used to direct the gas into the treatment space 5 as shown in EP 2 226 832 by applicant and hereby incorporated as reference. The gas supply device 8 may be provided with storage, supply and mixing components as known to the skilled person.

The gas directed to the treatment space for the nitration step is essentially consisting of N_2 (nitrogen) or NH_3 (ammonia) or NO or combination thereof. In further embodiments the gas composition may consist besides the presence of N_2 (nitrogen) or NH_3 (ammonia) or NO or combination thereof a small amount of H_2.

The total amount of gas supplied to the substrate for the nitridation step is in the range of 1 to 30 slm.

Further the temperature in the treatment space 5 during the nitridation step is preferably below 150^0C and even preferably below 100^0C ; the time of plasma treatment is preferably below the 10 minutes , preferably below 5 and even more preferably below 2 minutes. Excellent results have been found using at most 60 seconds of plasma treatment. As a result excellent barriers can be prepared at very mild conditions i.e. at atmospheric pressure at low temperature and high speed giving high economical value.

After the nitridation a substrate remains having a thin inorganic oxide film having a low N-atom concentration amount between 2 and 3%.

The nitrogen concentration is determined by X-ray Photoelectron Spectroscopy (XPS), using Amicon Electron Spectroscopy for Chemical Analysis (ESCA) equipment manufactured by Kratos.

Examples

Water vapour transmission rate (WVTR) of a typical 50 nm inorganic silicon oxide layer on a PEN 100 μm sheet film may change remarkably going from about 2 to about 0.002 g/m^2*day and typical barrier improvement factors after the plasma treatment is 400, 500 or 1000, which is an unforeseen and surprising effect. Barrier properties for such thin layers of comparable quality have previously only been reported for thin layers (about 50 nm) prepared by ALD (Atomic Layer Deposition) in a plasma process which is much less efficient and takes much more time as each atomic layer formed in an ALD cycle comprises 4 different steps.

WVTR is determined using a Mocon Aquatran Model 1 which uses a coloumetric cell (electrochemical cell) with a minimum detection limit of $5*10^{-4}$ g/m^2*day. This method provides a more sensitive and accurate permeability evaluation than the permeation measurement by using IR absorption. All measurements were done at 40°C/90%RH.

The free pore volume of the inorganic oxides was determined using the Lorentz-Lorenz equations by measuring the optical density difference of the material. Optical

density difference was measured using a Woollam Spectroscopic Ellipsometer equipped with an vacuum chamber and heating stage.

Several samples (rolls) were prepared by depositing PEN (100 μm thick) or PET (100 μm thick) using an atmospheric pressure glow discharge plasma apparatus as disclosed in WO 2009 104 957 in a treatment space using a plasma power of 600 W, an excitation energy of 200 kHz and a gas composition (95% N_2/5% O_2) using different precursors (HMDSO/TEOS) resulting in the following 12 examples all having 50 nm inorganic oxide (Silicon oxide) layer.

Table 1

	Substrate	Precursor	Pore (vol. %)
Example 1-4	PEN	HMDSO	0.4~3
Example 5-8	PET	HMDSO	0.3~2
Example 9-12	PET	TEOS	0.3~3

Typical WVTR of the PET samples after deposition is 5 g/m2*day and for PEN the WVTR is 2 g/m2*day. These WVTR values are similar to the values of the bare polymer film.

As next step a part of the 12 examples were treated using the same atmospheric pressure plasma apparatus (APGD) as described in WO 2009 104 957 using a plasma power of 300 W, an excitation energy of 200 kHz however as gas composition of

1) 100% N_2 (10 slm) or 2) 95% N_2+5%NH_3 (10 slm) or 3) 98% N_2+2%NO (10 slm) or 4) 90% N_2+10%H_2 (10 slm). The nitridation step was done in 60 seconds at a temperature of 90 ^{0}C.

Figure 2 shows N 1s signal of example 1 before and after the APGD nitridation step (post-treatment).

Another part of the same 12 examples were treated using a Low frequency (LF) dielectric barrier discharge (DBD) corona plasma using Softal corona unit type VTG 3005 (corona discharge treatment) equipment under the same gas compositions 1 - 4 described as above. Figure 3 shows the ESCA (XPS) result of the top surface of the corona N_2 treatment.

Table 2 shows the WVTR (in g/m^2*day) and barrier improvement factor (BIF) results for the 12 examples treated under the APGD or the corona treatment as nitidation step. The nitrogen atom concentration was determined on the examples after the APGD post-treatment.

Although in all cases an improvement of the barrier performance is observed the best results are obtained (even with a barrier improvement factor of about 1000) by using a high frequency APG discharge for the nitridation step.

Table 2

	Gas	APGD WVTR[@] (g/m^2*day)	APGD BIF	APGD N % [(*)]	Corona WVTR	Corona BIF
Example 1	N_2	0.003	666	1.3	1.0	2
Example 2	N_2/NH_3	<0.002	>1000	2.9	0.5	4
Example 3	N_2/NO	0.005	400	1.1	1.2	2
Example 4	N_2/H_2	0.003	666	1.6	0.8	2.5
Example 5	N_2	<0.002	>2500	2.2	3	1.7
Example 6	N_2/NH_3	<0.002	>2500	2.7	1.6	3
Example 7	N_2/NO	0.005	1000	1.8	3.9	1.3
Example 8	N_2/H_2	<0.002	>2500	2.1	2.0	2.5
Example 9	N_2	<0.002	>2500	2.5	3.1	1.6
Example 10	N_2/NH_3	<0.002	>2500	2.8	2.0	2.5
Example 11	N_2/NO	0.006	833	1.4	3.5	1.4
Example 12	N_2/H_2	<0.002	>2500	0.9	2.1	2.4

[(*)]: XPS reveals that as a result of the nitridation step a distinct low energy N1s peak appears which is attributed to N-Si3 bonding.

[(@)]: background signal has not been subtracted; as back ground signal is in the order of about 0.002 the WVTR of examples 2, 5, 6, 8, 9, 10, 12 are in fact lower than 0.002 which as been denoted as <0.002.

CLAIMS

1. A method for manufacturing a barrier layer on a substrate (1, 1a, 1b), the method comprising:

- providing a substrate (1, 1a, 1b) with an inorganic oxide layer having a pore volume between 0.3 and 10 vol. % ;

- treating said substrate with an inorganic oxide layer in a glow discharge plasma, said plasma being generated by at least two electrodes (2, 3) in a treatment space (5) formed between said two electrodes, said treatment space also being provided with a gas comprising Nitrogen compounds; and

- the treating of the substrate in said treatment space is done at a temperature below 150^0C, e.g. below 100^0C.

2. Method according to claim 1, wherein the treatment of the substrate is done until a barrier with a top layer comprising between 1 to 3% Nitrogen-atom concentration is formed.

3. Method according to claim 1 or 2, wherein the gas comprising Nitrogen compounds, comprises N_2 (nitrogen) and/or NH_3 (ammonia) and/or NO.

4. Method according to any of the preceding claims, wherein the gas comprising Nitrogen compounds has a pressure between 0.1 and 10 atmosphere, e.g. between 0.5 and 5 atmosphere, e.g. between 0.6 and 2 atmosphere or approximately 1 atmosphere.

5. Method according to any of the preceding claims, wherein the treating of the substrate (1, 1a, 1b) in said treatment space is done for a duration of less than 10 minutes, e.g. less than 5 minutes, e.g. less than 2 minutes, e.g. a duration of 60 seconds.

6. Method according to any of the preceding claims, wherein the substrate (1, 1a, 1b) is a flexible substrate, in particular a flexible polymeric substrate.

7. Method according to claim 6, wherein the electrodes (2,3) are roll-electrodes, and the flexible layer is moved through the treatment space (5) at a linear speed.

8. Method according to any of the preceding claims, wherein the inorganic oxide layer of the provided substrate (1, 1a, 1) is a silicon-oxide layer.

9. Method according to any of the preceding claims, wherein the top layer is between 5 and 15 nm, e.g. between 7 and 12 nm, thick.

10. Device for manufacturing a barrier layer on a substrate (1, 1a, 1b), the device comprising:

- at least two electrodes (2, 3), arranged to generate a glow discharge plasma in a treatment space (5) formed between said two electrodes;
- a gas supply device (8), arranged to provide a gas comprising Nitrogen compounds to the treatment space (5);
- wherein the treatment space if further arranged to hold and treat at least one substrate having an inorganic oxide layer, and the device is arranged for treating of the substrate in said treatment space at a temperature below 150^0C, e.g. below 100^0C.

11. Device according to claim 10, in combination with any of the features of claims 2-9.

12. Substrate (1, 1a, 1b) having a barrier layer, the barrier layer comprising an inorganic oxide layer having a pore volume between 0.3 and 10 vol. %, the inorganic oxide layer further having a top layer comprising between 1 to 3% Nitrogen-atom concentration.

13. Substrate (1, 1a, 1b) according to claim 12, wherein the inorganic oxide layer of the provided substrate is a silicon-oxide layer.

14. Substrate (1, 1a, 1b) according to claim 12 or 13, wherein the substrate (1, 1a, 1b) is a flexible substrate, in particular a flexible polymeric substrate.

15. Substrate (1, 1a, 1b) according to any of the claims 12-14, wherein the top layer is between 5 and 15 nm, e.g. between 7 and 12 nm, thick

Fig 1a

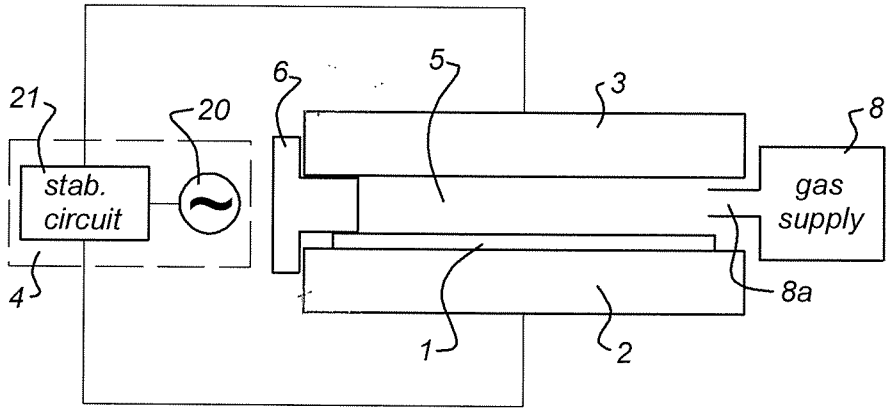
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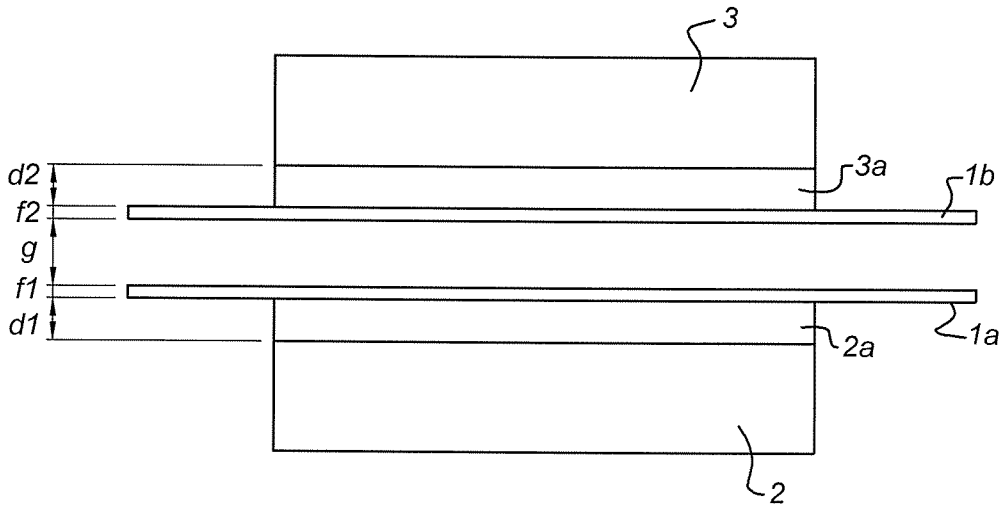
Fig 1b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2

Fig 1c

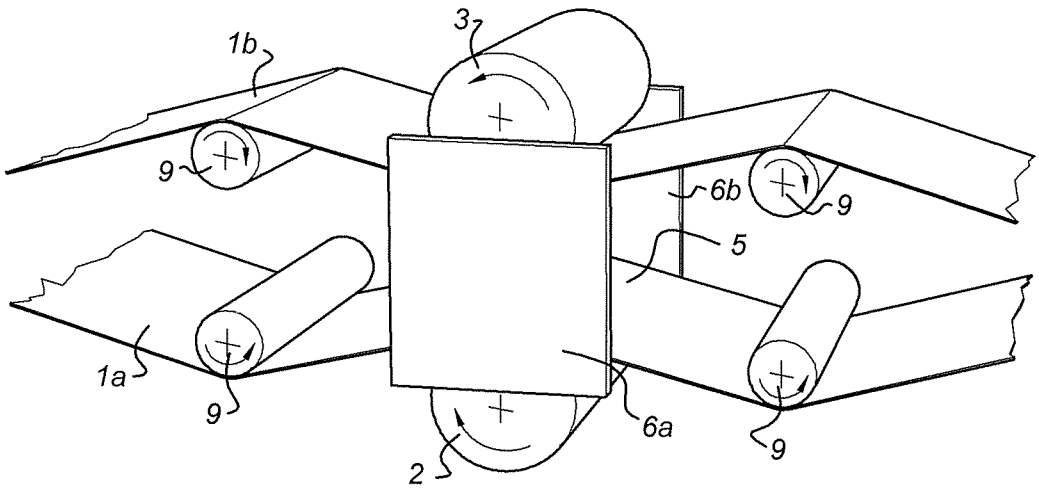
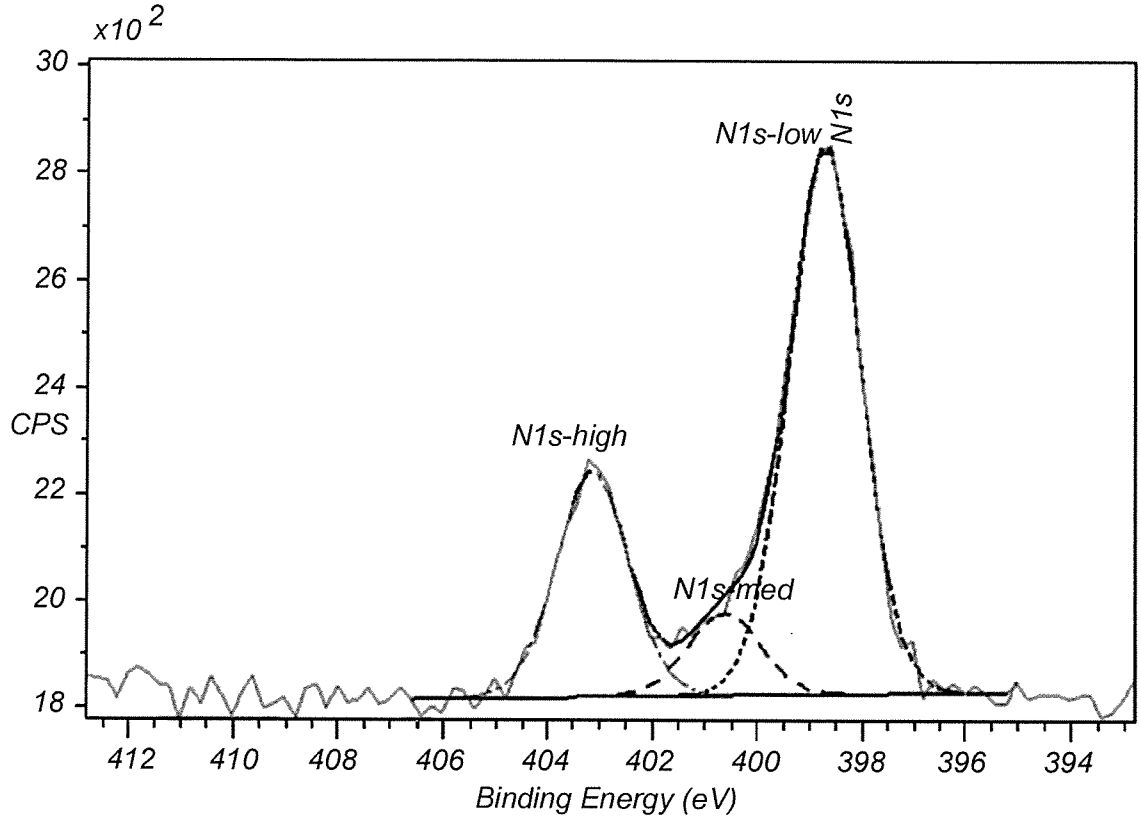


Fig. 2


x10 2
30
28
26
24
CPS
22
20
18
N1s-low
N1s
N1s-high
N1s-med
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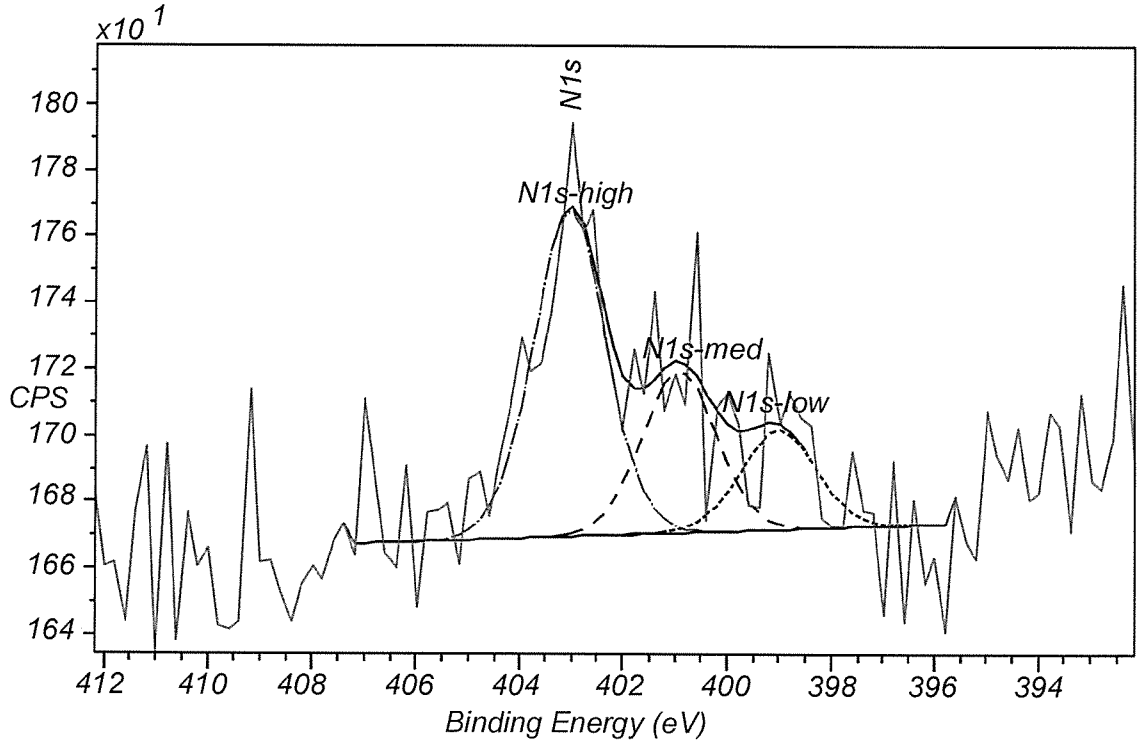
410
408
406
404
402
400
398
396
394
Binding Energy (eV)

Fig. 3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178
176
174
172
CPS
170
168
166
164
N1s
N1s-high
N1s-med
N1s-low
412
410
408
406
404
402
400
398
396
394
Binding Energy (eV)

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/050897

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/40 C23C16/56 H01J37/32 H01L21/314
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 H01J 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, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 1 403 902 A1 (FUJI PHOTO FILM BV [NL]) 31 March 2004 (2004-03-31) cited in the application	10,11
A	paragraphs [0004], [0039] - [0044]; example 2	1-9

A	HUA-GEN PENG ET AL: "Pore Sealing by NH[sub 3] Plasma Treatment of Porous Low Dielectric Constant Films", JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 154, no. 4, 1 January 2007 (2007-01-01), page G85, XP55038236, ISSN: 0013-4651, DOI: 10.1149/1.2435625 pages G90-G91, "Temperature dependence of pore sealing by plasma treatment"	1-9, 12-15

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

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 September 2012	24/09/2012

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	Patterson, Anthony

1

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006/148140 A1 (CHOU LIN-EN [TW] ET AL) 6 July 2006 (2006-07-06) paragraphs [0026] - [0028]; claims 10-18; figure 2	1-9, 12-15
A	US 2007/026243 A1 (IWANAGA HIROSHI [JP] ET AL) 1 February 2007 (2007-02-01) paragraphs [0148] - [0150]; table 1	12-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2012/050897

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP 4698310 B2	08-06-2011
		JP 2007015350 A	25-01-2007
		KR 20070007736 A	16-01-2007
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