



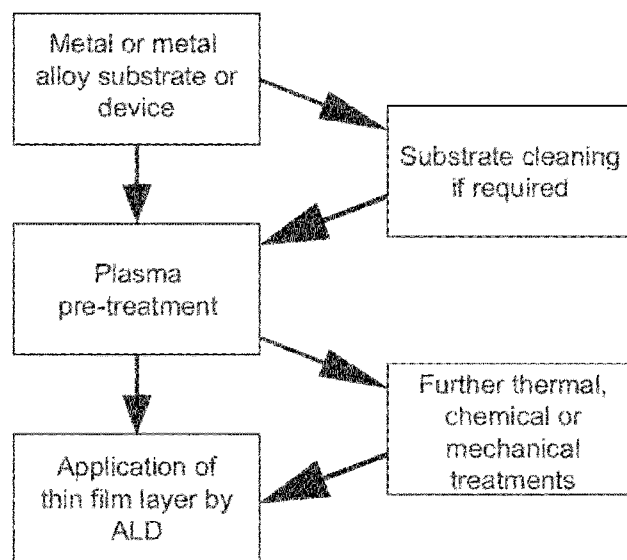
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(54) **Title:** PLASMA PRE-TREATMENT**FIG. 9**

(57) **Abstract:** A method of improved anti-corrosion properties of thin films is provided that includes using an argon-hydrogen (Ar-H₂) plasma to pre-treat a substrate, and using an atomic layer deposition (ALD) device to deposit a thin film on the substrate, where the ALD includes a thermal ALD or a plasma-enhanced ALD, and where the ALD includes a metal precursor and an oxygen source. The substrate can include a metal or metal alloy, and the thin film can include metal oxides, metal nitrides, metal carbides, or pure metals. The argon-hydrogen plasma pre-treatment can include a continuous or pulsed plasma, with exposure to ambient or no exposure to the ambient, and include either additional treatments or no additional treatments between the plasma pre-treatment and the ALD. Further, the thin film includes a thickness in the range of 0.1 nm to 10,000 nm.

PLASMA PRE-TREATMENT

FIELD OF THE INVENTION

The present invention relates generally to thin film coating. More particularly, the invention relates to pre-treatment for improving the anti-corrosion properties of thin films applied to metals or metal alloys.

BACKGROUND OF THE INVENTION

Corrosion is a major, global problem. In the United States the direct corrosion costs have been evaluated to have risen to over 3 % of the GDP annually. Careful attention to the corrosion prevention has to be given not only to manufacturing, but also to the constant monitoring, maintenance and repair of products in use. Most industries including oil and gas, automotive, aerospace, construction and biomedicine are forced to evaluate the costs of the material against the lifetime and costs of repair and maintenance of the product. One of the most popular methods for corrosion prevention is coating. Chromium-containing coatings dominated the field until recently. The restrictions issued on the use of chromium have stimulated a continuing search for replacements. Different coatings have been developed from several materials grown by various methods. It seems unlikely that a global solution that would replace chromium will be discovered. Thus, the development has to be concentrated on more specific solutions for each application.

Atomic layer deposition (ALD) is an interesting candidate for depositing corrosion protection coatings. Products that have complicated 3D surface morphologies or require careful surface control would be especially suitable for protection by ALD thin films. The promise of ALD lies in the growth mechanism. Precursors are delivered onto the substrate in the gas phase, alternately and separately from each other such that reactions occur only on the surface. The growth proceeds through nominally two separate surface reactions that are alternately repeated. Therefore, specific control of the deposition process and resulting film properties is ensured. The thickness of the film is determined through the number of cycles. Already at 2–10 nm thicknesses ALD Al_2O_3 thin films are known to have a low defect density.

Conformal and uniform films with controlled composition can be reliably deposited even on demanding high-aspect-ratio substrates. A combination of two or more materials into nanolaminates or mixed materials enables easy modification of the film properties. In the traditional thermal ALD process, precursors are simply evaporated and pulsed separately on the heated substrate. However, the reactivity of precursors can also be enhanced by activation with plasma as with plasma-enhanced ALD. Both thermal and plasma-enhanced ALD have their advantages and challenges.

Coatings made by thermal and plasma-enhanced ALD have been studied for corrosion protection on stainless steel, steel and aluminum. The results were encouraging; especially coatings that combined the good insulating properties of Al_2O_3 with the chemical durability of Ta_2O_5 showed great promise. Electrochemically-determined porosities of 0.06 – 0.44 % and complete protection for 4 hours in neutral salt spray testing were achieved with 60-120 nm thick films on carbon steel. However, with thermal

ALD the adhesion of the coatings to the substrate was found to be limited. Coatings on carbon steel and aluminum were observed to peel off during TEM sample preparation. This was not an issue with the PEALD coatings suggesting some beneficial effect of the plasma compared to the thermal ALD conditions.

Surface cleaning of metals and metal alloys by plasma treatment afforded improvement of adhesion, removal of organic contamination and activation through surface modification. Oxygen-containing plasmas are very efficient in removing organic residues from metal surfaces. However, surface oxide growth is simultaneously caused. Hydrogen-containing plasmas can also be used to clean the surface from organic residues. The cleaning is not as efficient as with oxygen, but the native oxide on the metal is simultaneously reduced enabling oxygen-free interfaces between the coating and the substrate. The optimum chemical state of the substrate prior to coating depends on the coating method, deposited material and the substrate itself. Formation of a nitrogen-rich layer on steel by nitrogen-hydrogen (N_2-H_2) or ammonia (NH_3) plasma pretreatment prior to TiN deposition by plasma-assisted chemical vapor deposition (PACVD) has been shown to improve the adhesion of the coating and surface hardness properties of the steel. With sol-gel coatings it has been found that the thicker oxide layer grown on metal surface by air plasma pretreatment enables growth of thicker films with good adhesion.

What is needed is a method of pre-treating a substrate material prior to thermal ALD to reduce organic contamination, improve coating adhesion and reduce the coating porosity.

SUMMARY OF THE INVENTION

To address the needs in the art, a method of improved anti-corrosion properties of thin films is provided that includes using an argon-hydrogen (Ar-H₂) plasma to pre-treat a substrate, and using an atomic layer deposition (ALD) device to deposit a thin film on the substrate, where the ALD includes a thermal ALD or a plasma-enhanced ALD, and where the ALD includes a metal (i.e., s-, d- or f-block) or p-block element precursor and an oxygen source.

According to one aspect of the invention, the substrate includes a metal or metal alloy. In another aspect the metal can include iron, carbon steel, stainless steel, crucible steel, alloy steel, spring steel, tool steel, aluminum, aluminum alloys, copper, copper alloys, magnesium, magnesium alloys, nickel, nickel alloys, cobalt, cobalt alloys, titanium, zirconium, tantalum, or lead.

According to a further aspect of the invention, the thin film can include metal oxides, metal nitrides, metal carbides, metal carbonates, metal silicides, metal silicates or pure metals. In one aspect, the film is a film stack, which comprises layers of different materials, or a film mixture, which comprises a solid solution of different materials.

In a further aspect of the invention, the argon-hydrogen plasma pre-treatment is applied for a duration in a range of 1 s to 1,000 s.

According to another aspect of the invention, the argon-hydrogen plasma pre-treatment includes a continuous or pulsed plasma.

In yet another aspect of the invention, the argon-hydrogen plasma pre-treatment comprises an exposure to ambient or no exposure to the ambient.

In a further aspect of the invention, the argon-hydrogen plasma pre-treatment either additional treatments or no additional treatments between the plasma pre-treatment and the ALD, where the additional treatments can include thermal treatment (heating), dry chemical treatments (such as etching with dry ice), wet chemical etching, mechanical treatments such as grinding, lapping, honing and polishing.

In a further aspect of the invention, the thin film includes a thickness in the range of 0.1 nm to 10,000 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGs. 1a-1f show time-of-flight secondary ion mass spectrometry ToF-SIMS depth profiles of carbon (C^-), hydroxyl (OH^-) and iron oxide (FeO_2^-) on untreated and H_2 -Ar plasma pre-treated 100Cr6 steel coated with 50 nm thermal ALD Al_2O_3 , according to one embodiment of the invention.

FIGs. 2a-2b show transmission electron microscopy cross sectional transmission electron microscope (TEM) images of 50 nm thermal ALD Al_2O_3

coatings on untreated and 60 min *in situ* plasma pre-treated 100Cr6 steel, according to one embodiment of the invention.

FIGs. 3a-3b shows polarization curves on untreated and *in situ* H₂-Ar plasma pre-treated 100Cr6 steel coated with 50 nm thermal ALD Al₂O₃, according to one embodiment of the invention.

FIG. 4 shows Tafel analysis results and the calculated porosities, according to one embodiment of the invention.

FIGs. 5a-5d show ToF-SIMS depth profiles of C⁻, OH⁻, FeO₂⁻ and CrO₂⁻ of untreated and plasma pre-treated 100Cr6 steel coated with 50 nm PEALD Al₂O₃, according to one embodiment of the invention.

FIGs. 6a-6c show TEM images of 50 nm PEALD Al₂O₃ coated steel without and with *in situ* plasma pretreatment, according to one embodiment of the invention.

FIG. 7 show polarization curves of 50 nm Al₂O₃ films deposited with PEALD on 100Cr6 steel, according to one embodiment of the invention.

FIG. 8 shows Tafel analysis and porosity calculation applied to the PEALD coatings, according to one embodiment of the invention.

FIG. 9 shows a flow diagram of the plasma pre-treatment and coating combination and optional extra cleaning or treatment steps, according to one embodiment of the invention.

FIGs. 10a-10c show variations of different embodiments of the pre-treatment method of the current invention.

DETAILED DESCRIPTION OF THE INVENTION

A method of argon-hydrogen plasma pre-treatment prior to thermal and plasma-enhanced

atomic layer deposition (ALD) of Al_2O_3 films on 100Cr6 steel for corrosion protection is provided. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and transmission electron microscopy (TEM) show the changes in the interface. The electrochemical properties of the samples with polarization measurements are provided, and the coating porosities calculated from the polarization results are presented for comparison of the coatings. Prior to thermal ALD the plasma pre-treatment reduces organic contamination, improve coating adhesion and reduce the coating porosity by 1 – 3 orders of magnitude. According to one embodiment of the invention, the anti-corrosion properties of the plasma-enhanced ALD (PEALD) coatings are improved by the pre-treatment where, after the plasma pre-treatment, the surface is given time to re-grow a thin protective interfacial oxide prior to exposure to the oxygen plasma before application of the PEALD Al_2O_3 coating. The different effects that thermal and plasma-enhanced ALD have on the substrate coating interface are compared. The reactivity of the oxygen precursor was shown to have a significant influence on the oxidation of the substrate surface in the early stages of film growth and thereafter also on the overall quality of the film.

According to one embodiment of the invention, plasma treatment of carbon steel prior to coating by thermal and plasma enhanced ALD is provided. The effect of the plasma pre-treatment on the substrate is presented and the most effective pre-treatment is provided to ensure good sealing properties and adhesion to the substrate. According to one aspect of the invention, the substrate includes a metal or metal alloy. In another aspect the metal can include iron, carbon steel, stainless steel, crucible steel, alloy steel, spring steel, tool steel, aluminum, aluminum alloys, copper, copper alloys, magnesium, magnesium alloys, nickel, nickel alloys, cobalt, cobalt alloys, titanium, zirconium, tantalum, or lead. Argon-

hydrogen plasmas with different pre-treatment times and different plasma equipment are provided. In one aspect, a reducing plasma pre-treatment was chosen to remove carbonaceous impurities while simultaneously avoiding enhanced interface oxidation.

The effect of exposure to the ambient air after the pre-treatment and prior to coating was also investigated. Some coatings were deposited without (*in situ* pre-treatments) and some with (*ex situ* pre-treatments) exposure to air. According to other embodiments of the invention, the thin film can include metal oxides, metal nitrides, metal carbides, or pure metals. Other examples include, TiO_2 , Ta_2O_5 , SiO_2 , ZrO_2 , TiN , WC , Si , Pt , Ru , etc. In one aspect, the film is a film stack, which comprises layers of different materials, or a film mixture, which comprises a solid solution of different materials.

ALD Al_2O_3 thin films were used in included examples as a model coating even though it is understood that Al_2O_3 alone does not give the optimum corrosion protection. However, Al_2O_3 can be grown very reliably and consistently with different ALD reactors. It also has good insulating properties, enabling easy comparison of electrochemical properties after different plasma pre-treatments. The knowledge gained with ALD Al_2O_3 about plasma pre-treatment can thereafter be utilized for other ALD corrosion protection coatings with composition and multilayer structure optimized for the best protective properties.

According to one embodiment, the substrate material was hardened and tempered carbon

steel (100Cr6, AISI 52100). The alloying elements of the steel were C (0.95-1.1 w%), Cr (1.5 w%), Ni (max. 0.30 w%), Mn (0.25-0.45 w%), Cu (max. 0.30 w%), Si (0.15-0.35 w%), P (max. 0.030 w%) and S (max. 0.025 w%). The steel surfaces were lapped in a water-based diamond suspension (6 μm). According to the invention, the substrate can include sheet metal or mechanical components.

Embodiments of hydrogen-argon ($\text{H}_2\text{-Ar}$) plasma pre-treatments were carried out with and without exposure to the ambient. Prior to plasma pre-treatment or coating (untreated samples) the substrates were cleaned. The samples were cleaned by ultrasonication in acetone for 5 min prior to ultrasonication in isopropanol, rinsing with ethanol and blow-drying with compressed air. Reactors in a cleanroom (ISO class 6) and outside a cleanroom were used. During the pre-treatments the reactor temperature was maintained at 150 °C. In one aspect of the invention, the argon-hydrogen plasma pre-treatment is applied for a duration in a range of 1 s to 1,000 s. According to another aspect of the invention, the argon-hydrogen plasma pre-treatment includes a continuous or pulsed plasma. In a further aspect of the invention, the argon-hydrogen plasma pre-treatment has either additional treatments or no additional treatments between the plasma pre-treatment and the ALD, where the additional treatments can include thermal treatment (heating), dry chemical treatments (such as etching with dry ice), wet chemical etching, mechanical treatments such as grinding, lapping, honing and polishing.

In one example, the plasma was generated by an inductively-coupled plasma (ICP) source operated at 13.56 MHz in a remote plasma configuration. For these examples, the plasma power was 300 W, except for the 60 min pre-treatments, where 150 W was used. The base pressure was <1 mTorr and typical operating pressures were 100 – 500 mTorr,

although during the plasma pretreatments the pressure was ~100 mTorr. Hydrogen (50 sccm, >99.999%) and argon (50 sccm, >99.999%) were flowed into the reactor for 10 s before plasma was applied. For pre-treatments where the substrate was not exposed to the ambient, a 10 s argon (50 sccm) purge was used to separate the pre-treatment and deposition. This purge was extended to 10 min for experiments with plasma-enhanced ALD.

The *ex situ* experiments involved venting and opening the reactor for 2 min to cleanroom air. The metal substrates were not removed from the heated substrate holder in order to avoid effects of handling.

For the experiments in non-cleanroom conditions, the reactor temperature was maintained at 160 °C during the pre-treatments. The plasma was generated with a capacitively-coupled (CCP) source operated at 13.56 MHz. The reactor was operated in remote plasma configuration with a grid, which acted as the bottom electrode, separating the active plasma from the substrates. The distance from the grid to the substrates was 4 cm. Plasma powers between 100 – 300 W were used. The operating pressure was maintained between 4 and 8 Torr with an argon inert gas flow. Prior to mixing the plasma gases, hydrogen (>99.999%) and argon (>99.999%) were purified on site. In the *in situ* experiments the reaction space was purged with nitrogen (>99.999%) for 15 min between the pre-treatment and coating deposition. Argon was used as the inert process gas. Long 30 min *in situ* and *ex situ* pre-treatments were conducted by ALD-type pulsing, because the temperature increase in the reactor prohibited the use of a continuous H₂-Ar plasma for more than 5 min. Hydrogen and argon were constantly flowed over the substrates, but the plasma power was on for 5 s (pulse) and off for 10 s (purge). This cycle was repeated

such that the total time of exposure to plasma species was 30 min. The *ex situ* experiments were conducted by cooling the reactor to 100 °C after the pre-treatment, venting to laboratory air and moving the samples to another ALD reactor. The samples were exposed to laboratory air for approximately 2-3 min. Details for all pre-treatments are presented in **Table I**.

Table I. Experimental details for the plasma pre-treatments.

Cleanroom?	Exposure to Ambient	Plasma gas flow rates / sccm		Pre-Treatment Time / min	Plasma Power /W	Waiting time prior to ALD deposition
		H ₂	Ar			
Yes	n/a	50	50	0 (no pre-treatment)	-	-
Yes	No	50	50	5	300	10 s
Yes	No	50	50	30	300	10 s
Yes	No	50	50	60	150	10 s
Yes	Yes	50	50	30	300	-
No	n/a	n/a	n/a	0 (no pre-treatment)	-	-
No	No	30	130	5	300	15 min
No	No	15	130	30	100	15 min
No	Yes	15	130	30	170	-
Yes	n/a	n/a	n/a	0 (no pre-treatment)	-	-
Yes	No	50	50	30	300	10 s
Yes	No	50	50	30	300	10 min
Yes	Yes	50	50	30	300	-

Regarding embodiments with additional treatments between the plasma pre-treatment and the ALD, other oxygen sources than O₂, H₂O, O₃ are: NO, N₂O, NO₂, N₂O₄, N₂O₅, H₂O₂, alcohols (ROH), aldehydes (RCOH), ketones (RCOR'), esters (RCOOR'), ethers (ROR'), carboxylic acids (RCOOH), organic peroxides (ROOR'), organic amides (RCONR'R''), acid anhydrides (RCOOCOR') or acid halides (RCOX). In all cases R, R' and R'' =

hydrogen or a linear or branched alkyl group containing 1 to 10 carbon atoms. R, R' and R'' can be the same or different. R, R' and R'' can be aliphatic or aromatic. X = any halogen. The oxygen sources can be used individually or as a mixture. The oxygen sources can either be applied as they are or in the form of a plasma.

Nominally 50 nm thick Al_2O_3 thin films were used as corrosion protection coatings in these examples. According to the embodiments of the invention, the thin film can have a thickness in the range of 0.1 nm to 10,000 nm. The metal precursor was trimethyl aluminum ($\text{Al}(\text{CH}_3)_3$, TMA). Water or an O_2 plasma was used as the oxygen precursor.

According to one aspect of the invention, the ALD includes a metal (i.e., s-, d- or f-block) or p-block element precursor and an oxygen source.

Details on all the deposition processes are presented in **Table II**. The number of cycles was chosen so as to obtain the 50 nm coating thickness.

Table II. Experimental details for the ALD and PEALD film deposition and growth

Activation	Temperature /°C	$t_1-t_2-t_3-t_4^*$ /s	Growth rate / nm/cycle
Thermal	150	0.05 – 5 – 0.02 – 10	0.09
Thermal	160	0.3 – 15 – 0.35 – 15	0.10
Thermal	160	0.1 – 5 – 0.1 – 5	0.09
Plasma	150	0.05 – 5 – 4 – 2	0.13

The times t_1 , t_2 , t_3 and t_4 correspond to TMA pulse, purge, H_2O or O_2 pulse and purge, respectively.

The composition of the coatings and the coating-substrate interface were studied with time-of-light secondary ion mass spectrometry. Negative ion profiles were recorded, because they are more sensitive to fragments originating from oxide matrices.

Transmission electron microscopy (TEM) was used for cross sectional imaging of the samples.

The anti-corrosion properties of the coatings were evaluated by electrochemical polarization measurements (linear sweep voltammetry, LSV). The measurements were conducted at ambient temperatures in a traditional three-electrode cell with platinum as the counter-electrode and a standard calomel reference electrode (SCE). The working electrode area was restricted to 0.44 cm² with an O-ring. The electrolyte solution was de-aerated 0.2 M sodium chloride (NaCl, Analar Normpur analytical reagent VWR® BDH Prolabo®). The de-aeration was carried out by argon bubbling for 30 min prior to the measurement and continuing the bubbling during the measurement. The polarization experiment was started with 30 min stabilization at the open circuit potential (OCP). For more specific analysis of the coating differences, Tafel analysis was applied on the polarization curves.

For experiments carried out under cleanroom condition, a continuous plasma was used and the coating deposition was started 10 s after the pre-treatment for samples not exposed to the ambient. For samples that were exposed the ambient, the transfer time was 2 min without handling the samples. For non-cleanroom conditions, a pulsed plasma (5 s on, 10 s off) was used for the 30 min pre-treatments, and there was a 15 min waiting time

between the *in situ* pre-treatments and coating deposition. The ambient exposure was 2-3 min to normal laboratory air while the samples were moved to another ALD reactor.

After plasma pre-treatment thermal ALD was used to grow nominally 50 nm thick Al_2O_3 coatings on 100Cr6 steel. All coatings were measured to be 50 ± 4 nm thick on silicon.

Time-of-flight secondary ion mass spectrometry ToF-SIMS depth profiles of carbon (C^-), hydroxyl (OH^-) and iron oxide (FeO_2^-) on untreated and H_2 -Ar plasma pre-treated 100Cr6 steel coated with 50 nm thermal ALD Al_2O_3 are shown in **FIGs. 1a-1f**. Here, ToF-SIMS C^- , OH^- and FeO_2^- depth profiles for untreated and 5, 30 and 60 min *in situ* and 30 min *ex situ* H_2 -Ar plasma pre-treated 100Cr6 steel coated with 50 nm thermal ALD Al_2O_3 are presented. **FIGs. 1a-1c** presents results for cleanroom conditions and **FIGs. 1d-1f** for non-cleanroom conditions. The coating and interface regions can be clearly distinguished. The starting point of the interface region is taken as the point where FeO_2^- and other native oxide signals (not shown here) start to increase. This point is marked with a dashed line across the images.

The pre-treatments carried out under cleanroom conditions are first considered (**FIGs. 1a-1c**). All pre-treatments reduced the OH^- impurities in the bulk coating, but did not affect the C^- content (**FIGs. 1a** and **1b**). Hydroxyl groups in dense ALD oxide films are generally thought to originate from incomplete deposition reactions, but if the films are left porous, hydroxyl groups may also arise from water uptake during storage in air after the film growth. The decreased bulk OH^- concentration most likely indicates decreased water absorption after the growth. The water uptake is known to correlate with film density: the lower the density, the more defects there are for water to penetrate and absorb

into the oxide matrix. Thus the lower bulk OH^- concentration implies that the porosity of the Al_2O_3 is lower in samples plasma pre-treated prior to coating. FeO_2^- could not be detected in the coating region indicating that there were no such holes in the coating that would have exposed the bare substrate (**FIG. 1c**). The coating was defect-free in the detection limit of the ToF-SIMS equipment used.

C^- , OH^- and FeO_2^- peaked at the interface of the untreated sample (**FIGs. 1a-1c**). Where pre-treated samples were not exposed to the ambient, the OH^- peak was absent and the FeO_2^- peaks had a lower intensity than the untreated sample. Some decrease of the interfacial C^- contamination could also be detected. The changes were more pronounced by increasing the pre-treatment time up to 30 min. The interfacial compositions obtained with the 30 and 60 min pre-treatments were similar. The results imply that the plasma pre-treatment removed some organic contamination from the surface and reduced the native oxide layer of the steel. The remaining oxide layer was also changed in composition. The original hydroxyl impurity concentration was significantly reduced.

The samples which were exposed to cleanroom air after the otherwise same pre-treatment as those which were not, re-growth of the interfacial oxide layer modified or reduced by the pre-treatment was observed (**FIGs. 1a-1c**). The OH^- peak reappeared and the FeO_2^- intensity increased again, but the intensities were still lower than for the untreated sample. The C^- intensity was approximately at the same level for the *in* and *ex situ* pre-treated samples indicating that the 2 min exposure to cleanroom did not recontaminate the surface with organic species.

The pre-treatments carried out in normal laboratory conditions reduced both C^- and OH^-

impurities in the bulk coating (**FIGs. 1d** and **1e**). The C⁻ contamination in the near interface region of the coating was especially affected, which suggests an improved nucleation period for the film growth.

As with the cleanroom samples, FeO₂⁻ could not be detected in the coating region (**FIG. 1f**). On the untreated sample, C⁻, OH⁻ and FeO₂⁻ peaked at the interface (**FIGs. 1d-1f**). In contrast to the cleanroom samples, only C⁻ was substantially reduced by the *in situ* pre-treatments (**FIG. d**). The OH⁻ and FeO₂⁻ intensities were slightly smaller in the *in situ* pre-treated samples, but the change was not as pronounced as for the cleanroom samples (**FIGs. 1e** and **1f**). Likely causes for these differences are the pulsed plasma used for the pre-treatment and the 15 min waiting time prior to coating deposition after the non-cleanroom *in situ* pre-treatments (**Table I**). The substrate surfaces had time to re-grow an oxide layer prior to coating. The coating in the cleanroom was started 10 s after the *in situ* pre-treatment leaving only little time for reformation of an oxide layer. Another possible explanation is the higher ion flux in this case, which might have led to more efficient interface oxide reduction. The *ex situ* pre-treatment involved exposure to laboratory air after the otherwise same 30 min pre-treatment that was carried out *in situ* in non-cleanroom conditions.

Approximately 50 s longer sputtering time was required to reach the interface. This was due to a more pronounced carbon contamination layer on the coating surface compared to the other samples. The reasons for the formation of this layer are unknown. The data points for the *ex situ* sample in **FIGs. 1a-1f** are presented so that the interfaces start after the same sputtering time in all samples. The “excess” sputtering time is presented by showing the C⁻, OH⁻ and FeO₂⁻ intensities on the negative sputtering time. This enables

easier comparison of the pre-treatment effects. The *ex situ* pre-treatment resulted in enhanced oxidation of the substrate surface (**FIGs. 1d-1f**). The OH^- and FeO_2^- peaks were higher in intensity and wider than in the untreated sample. This is consistent with the observed reappearance of the OH^- peak and intensified FeO_2^- peak in the *ex situ* pre-treatments. No differences could be observed in the interfacial carbon contamination in the *in* and *ex situ* pre-treated samples. This indicates that significant recontamination with organic species was avoided also with *ex situ* exposure to laboratory air.

Transmission electron microscopy cross sectional transmission electron microscope (TEM) images of 50 nm thermal ALD Al_2O_3 coatings on untreated and 60 min *in situ* plasma pre-treated 100Cr6 steel are shown in **FIGs. 2a-2b**. Here, TEM images are provided of 50 nm Al_2O_3 on a 100Cr6 steel substrate deposited using (**FIG. 2a**) thermal ALD with no pre-treatment and (**FIG. 2b**) thermal ALD with a 60 min *in situ* H_2 -Ar plasma pre-treatment. The ALD coatings appear to be amorphous and defect-free, as expected. Some voids could be observed between the coating and the untreated steel substrate indicating problems with adhesion (**FIG. 2a**). This observation is in line with the adhesion problems observed with thermal ALD coatings on steel and aluminum previously. The coating on the 60 min *in situ* plasma pre-treated substrate was well adhered (**FIG. 2b**). Such an improvement of the adhesion was observed on all the plasma pre-treated samples studied with TEM. The improved adhesion was probably due to the decreased amount of organic impurities on the steel surface. As ALD films grow via chemical reactions of precursors with a surface, an organic contamination layer, which does not have proper surface groups for the film growth, can result in poor quality films, at least in the early stage of the film growth. This theory is supported by the decrease of carbon and hydroxyl impurities in the ALD films after the plasma pre-treatments as

observed with ToF-SIMS. An approximately 5 nm thick interfacial layer could be observed between the coating and substrate in both the untreated and pre-treated sample (**FIGs. 2a-2b**). This layer corresponds to the interfacial oxide layer observed with ToF-SIMS.

Polarization curves on untreated and *in situ* H₂-Ar plasma pre-treated 100Cr6 steel coated with 50 nm thermal ALD Al₂O₃ are presented in **FIGs. 3a-3b**. In all the samples pre-treated under cleanroom conditions the corrosion current density was lower compared to the untreated sample indicating lower corrosion rates (**FIG. 3a**). A decrease of the current density with pre-treatment time could also be observed. However, the pre-treated samples had a lower corrosion potential than the untreated sample, and thus a narrower cathodic potential range. Changes in the Fe³⁺/Fe²⁺ ratio in the interfacial oxide layer have an influence on the steel surface potential. Thus the reducing *in situ* pre-treatment probably had an effect on the electrochemical properties of the steel. This is confirmed by the partial reduction of the steel after the *in situ* pre-treatments observed with ToF-SIMS. With the 5 and 30 min pre-treated samples, an increase of current density at the anodic potential range was observed at lower potentials. Therefore those pretreatments slightly narrowed the stable potential range that was achieved with the ALD Al₂O₃ coating without pre-treatment.

Also the *in situ* pre-treatments carried out under laboratory conditions decreased the corrosion current density compared to the untreated sample (**FIG. 3b**). The current density decreased with increasing pre-treatment time. Corrosion potentials could not be extracted from the data due to the high level of noise and low current density at the cathodic potential range. In contrast to the cleanroom samples, the increase of the current

density in the pre-treated samples at the anodic potential range started at higher potential than in the untreated samples. Thus, a wider stability range was achieved with the plasma pre-treatments under normal laboratory conditions.

Film porosities (P), which represent the uncoated surface fraction of the substrate, were calculated to allow easier comparison of the pre-treatments.

$$P = \frac{i_{corr}}{i_{corr}^0} \times 100\% \quad [1]$$

where i_{corr}^0 and i_{corr} present the corrosion current densities of the uncoated sample and the coated sample under evaluation, respectively. Tafel analysis results and the calculated porosities for untreated and H₂-Ar plasma pre-treated 100Cr6 steel coated with 50 nm thermal ALD Al₂O₃ are presented in **Table III** and **FIG. 4**. All the plasma pre-treatments reduced the corrosion current density and porosity of the coated steel, as already observed from the polarization curves. For the *in situ* pre-treatments the porosity was inversely proportional to the pre-treatment time. The porosities of the pre-treated samples under normal laboratory conditions were lower than the corresponding samples pre-treated under cleanroom conditions. The porosities after 5 and 30 min were 0.16 and 0.10 % (cleanroom), and 0.018 and 0.0053 % (laboratory).

Table III. Tafel analysis results and calculated porosities for 50 nm thermal ALD Al₂O₃ coatings deposited on untreated and plasma pre-treated 100Cr6 steel.

Pre-Treatment Time	Conditions	Exposure to Ambient	Corrosion current density / $\times 10^{-9} \text{ A cm}^{-2}$	Porosity / %
Bare 100Cr6 steel	n/a	n/a	430	100
No pre-treatment	Cleanroom	n/a	0.82	0.19
5 min	Cleanroom	no	0.69	0.16
30 min	Cleanroom	no	0.43	0.10
60 min	Cleanroom	no	0.30	0.070
30 min	Cleanroom	yes	0.22	0.052
No pre-treatment	Non-cleanroom (laboratory)	n/a	1.0	0.23
5 min	Non-cleanroom (laboratory)	no	0.076	0.018
30 min	Non-cleanroom (laboratory)	no	0.023	0.0053
30 min	Non-cleanroom (laboratory)	yes	0.42	0.099

The only differences observed in the samples with ToF-SIMS were in the hydroxyl and oxide intensities at the interface (**FIGs. 1a-1f**). ALD Al₂O₃ growth is known to start preferentially on surface hydroxyl groups. The removal of active surface species might hinder proper nucleation of the film locally resulting in slight decrease of the sealing

properties of the coating.

With *ex situ* pre-treatments lower porosities were obtained under cleanroom conditions than under normal laboratory conditions (**Table III** and **FIG. 4**). Experiments under cleanroom conditions where samples were exposed to the ambient between pre-treatment and coating resulted in lower porosities than with no ambient exposure. This gives support to the theory that the hydroxyl-depleted surface is not an ideal starting surface for thermal ALD of Al_2O_3 .

The effect of H_2 -Ar plasma pre-treatment was also studied with Al_2O_3 coatings deposited with PEALD under cleanroom conditions only (**Tables I** and **II**). Plasmas were applied for 30 min prior to coating. For samples not exposed to the ambient, the waiting time after the pre-treatment was either 10 s or 10 min. The results were compared to a PEALD coating deposited without plasma pre-treatment. All the PEALD coatings were measured to be 50 ± 4 nm thick on silicon.

ToF-SIMS depth profiles of C^- , OH^- , FeO_2^- and CrO_2^- of untreated and plasma pre-treated 100Cr6 steel coated with 50 nm PEALD Al_2O_3 are presented in **FIGs. 5a-5d**. A slight reduction of OH^- impurities in the bulk coating was achieved with the plasma pre-treatments (**FIG. 5b**), but no effect on the carbon impurities could be observed (**FIG. 5a**). Neither FeO_2^- nor CrO_2^- could be detected in the coating region (**FIGs. 5c-5d**). The improvements to the bulk coating achieved with plasma pre-treatment were similar for the PEALD and thermal ALD coatings. C^- , OH^- , FeO_2^- and CrO_2^- peaked at the interface of the untreated sample (**FIGs. 5a-5d**). The impurity levels were approximately at the same level as in the untreated steel coated with thermal ALD. The interfacial C^- contamination

was reduced by the *in situ* pre-treatments (**FIG. 5a**). The intensity peaked two times in the sample with 10 s waiting time. This was mirrored by the OH^- and CrO_2^- signals. The FeO_2^- intensity increased substantially throughout the interface region compared to the untreated sample. In the sample made with the 10 min waiting time the interface layer was significantly decreased compared to the 10 s waiting time, but still larger than in the untreated sample. C^- and OH^- contamination intensities were lower than in the untreated sample and the FeO_2^- and CrO_2^- species only slightly surpassed it. PEALD deposition 10 s after the plasma pre-treatment clearly caused substantial growth of an interface oxide layer, so much so that the samples looked oxidized to the naked eye. The composition of the interface layer was not just a single Fe-Cr-O layer similar to the other samples, but seemed to have also an iron-oxide-enriched layer on top. This was probably due to steel surface activation by the pre-treatment. Exposure of the pristine surface to the extremely reactive oxygen plasma species resulted in a fast initial build-up of an interfacial oxide layer. The thickness or density of this layer was higher than in the other samples as the sputtering time required to reach the bulk of the substrate was substantially longer. In the untreated sample the native oxide layer appeared to shield the surface from the reactive plasma species, and its removal rendered the surface vulnerable to facile oxidation. The oxide could reform when the heated substrate was held under vacuum for a sufficient time or when the substrate was exposed to air. The lowest OH^- , FeO_2^- and CrO_2^- intensities at the interface were obtained with the *ex situ* pre-treatment (**FIGs. 5b-5d**). The C^- intensity was approximately the same for the untreated and *ex situ* pre-treated samples (**FIG. 5a**).

TEM images of 50 nm PEALD Al_2O_3 coated 100Cr6 steel without and with *in situ* plasma pretreatment are presented in **FIGs. 6a-6c**. All coatings appeared conformal, defect-free and well adhered to the substrate. Unlike with the thermal ALD coating on untreated

steel no problems with adhesion could be observed with the PEALD coating on untreated steel. An interlayer of approximately 4 nm thickness was observed between the untreated substrate and the coating (**FIG. 6a**). Application of 30 min plasma pre-treatment with a 10 s waiting time resulted in a significantly thicker interlayer of 15 – 35 nm in thickness (**FIG. 6b**). The interlayer thickness was reduced substantially to approximately 7 nm by extending the wait time to 10 min (**FIG. 6c**). The TEM images confirmed the observations and conclusions made from the ToF-SIMS results. Direct exposure of the plasma-activated steel surface to reactive species like an oxygen plasma induces an interfacial oxide layer growth on the substrate. Allowing some deactivation (oxidation) of the surface prior to coating minimizes the effect. It should also be noted that the interface thickness on the 10 min waiting time sample was still thicker than any interface oxide in the pre-treated samples coated with thermal ALD.

Polarization curves of 50 nm Al_2O_3 films deposited with PEALD on 100Cr6 steel are presented in **FIG. 7**. *In situ* pre-treatment with 10 s waiting time resulted in higher corrosion current density compared to the untreated sample. This implies that the thick interface oxide layer that formed when the steel surface, from which the pre-treatment plasma had stripped off the native oxide, was exposed to active oxygen species in PEALD hindered the protective qualities of the coating. The corrosion potential was very close to the untreated sample confirming that any reduction of the interfacial oxide obtained with the plasma pre-treatment was lost after the almost immediate exposure of the surface to oxygen plasma species. The *in situ* pre-treatment with 10 min waiting time resulted in a significantly lower corrosion current density. The pretreatment also caused the corrosion potential to disappear under noise in the current, although an earlier increase of current density at the anodic potential range could be observed indicating a narrower stable

potential range.

Tafel analysis and porosity calculation was applied also to the PEALD coatings according to Equation 1 and presented in **Table IV** and **FIG. 8** (Note the break in the vertical axis). For experiments without ambient exposure, the sample with 10 s waiting time resulted in a significantly higher porosity than the untreated and treated sample with longer waiting time. The lowest porosity obtained with PEALD Al_2O_3 was achieved with the pre-treatment with ambient exposure, which further confirmed the positive effect on the sealing property of a sufficient interface oxide layer on the steel prior to film growth by PEALD.

FIG. 9 shows a process flow diagram for the proposed plasma pre-treatment and coating combination, including optional extra cleaning or treatment steps, where the metal can undergo plasma pre-treatment directly or undergo a cleaning process prior to the plasma pre-treatment, and the pre-treated metal can have an ALD coating applied directly thereafter, or undergo further chemical or mechanical treatments prior to the application of a thermal ALD coating.

FIGs. 10a-10c show variations of different embodiment of the pre-treatment method according to the current invention. **FIG. 10a** shows the transfer of the pre-treated substrate through the ambient to the ALD reaction reactor, **FIG. 10b** shows the transfer of the pre-treated substrate without exposure to the ambient, and **FIG. 10c** shows application of the ALD film directly after the argon-hydrogen plasma pre-treatment in the same reactor.

Table IV. Tafel analysis results and calculated porosities for 50 nm PEALD Al₂O₃ coatings deposited on untreated and plasma pre-treated 100Cr6 steel.

Sample	Exposure to Ambient	Corrosion current density $/ \times 10^{-9} \text{ A cm}^{-2}$	Porosity / %
Bare 100Cr6 steel	n/a	430	100
No pre-treatment	n/a	0.91	0.21
30 min pre-treatment with 10 s waiting time	no	12	2.7
30 min pre-treatment with 10 min waiting time	no	0.68	0.16
30 min pre-treatment	yes	0.23	0.053

The influence of H₂-Ar plasma pre-treatment with and without ambient exposure on the corrosion protection properties of 50 nm Al₂O₃ coatings deposited with thermal and plasma-enhanced ALD on carbon steel was studied. The corrosion protection properties of coatings deposited with both methods could be improved with plasma pre-treatment, although the improvement was more pronounced for thermal ALD coatings. Adhesion to the substrate was increased and coating porosity reduced. The improvement increased with pre-treatment time.

The H₂-Ar plasma pre-treatment was found to reduce and modify the native oxide of steel and to remove organic residues. The hydrocarbon removal resulted in improved nucleation of the film and thereby reduced the porosity of the coating. It also improved

the adhesion of the coating. The composition and thickness of the interfacial oxide layer proved to have a decisive effect on the coatings and the overall corrosion behavior. The best protective properties were achieved with coatings deposited on a clean and uniform oxide that was re-grown after the plasma pre-treatment, but before the ALD process. This was achieved either by exposing the samples to air i.e. *ex situ* conditions after the pre-treatment, or by giving sufficient waiting time for the surface to react with residual gases between the *in situ* pretreatment and coating. The mechanism behind the beneficial effect of the re-grown oxide layer appeared to be different in thermal ALD and PEALD coatings, which could be attributed to the reactivity of the oxygen-sources in the coating process. In thermal ALD the re-grown oxide offered a better surface for nucleation thus reducing the number of defects in the coating. By contrast, in PEALD the re-grown oxide protected the steel surface from the highly reactive oxygen plasma used as a precursor. A steel surface from which the native oxide had been stripped with the plasma pre-treatment, and had not been allowed to re-grow, was oxidized in the PEALD process more extensively, forming a thicker spurious oxide layer with a detrimental effect on the protective qualities of the coating. Thus the protective qualities of the coatings are interface-dependent, which also relates to whether pre-treatments with or without exposure to the ambient should be used with thermal ALD and PEALD. With either of these pre-treatments excellent results could be obtained when a clean and uniform interface oxide was allowed to re-grow before the deposition. Furthermore, it is expected that the conclusions made about plasma pre-treatment of steel before Al_2O_3 deposition can be exploited also for other materials grown with thermal ALD and PEALD.

The present invention has now been described in accordance with several exemplary embodiments, which are intended to be illustrative in all aspects, rather than restrictive.

Thus, the present invention is capable of many variations in detailed implementation, which may be derived from the description contained herein by a person of ordinary skill in the art. For example, whether or not exposure to the ambient is required, whether a cleanroom is required, the pre-treatment time, the types of plasma used, the plasma power, additional surface treatments used, the type of substrate required, the type of coating material, and the thickness of the coating films.

All such variations are considered to be within the scope and spirit of the present invention as defined by the following claims and their legal equivalents.

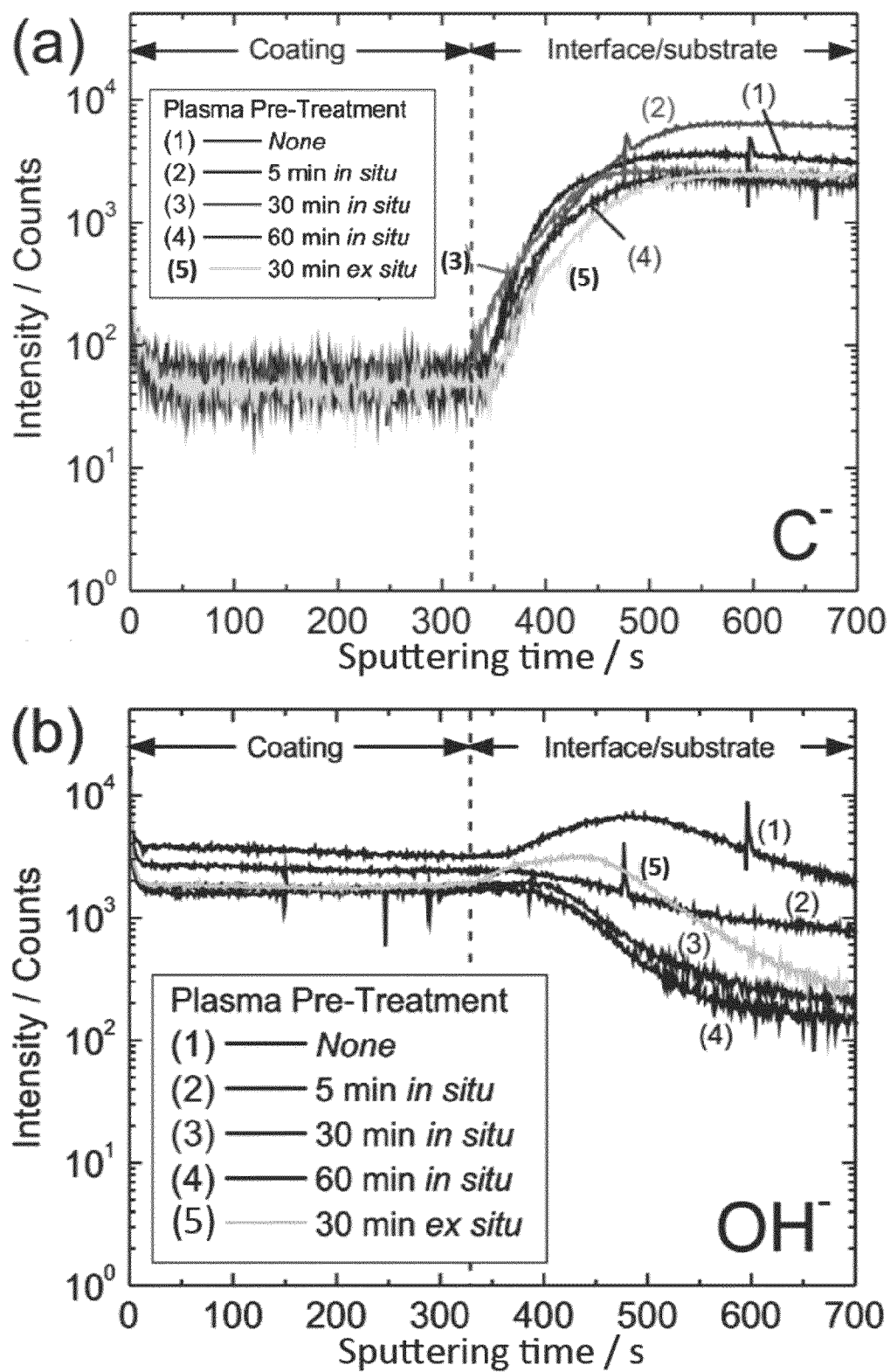
CLAIMS

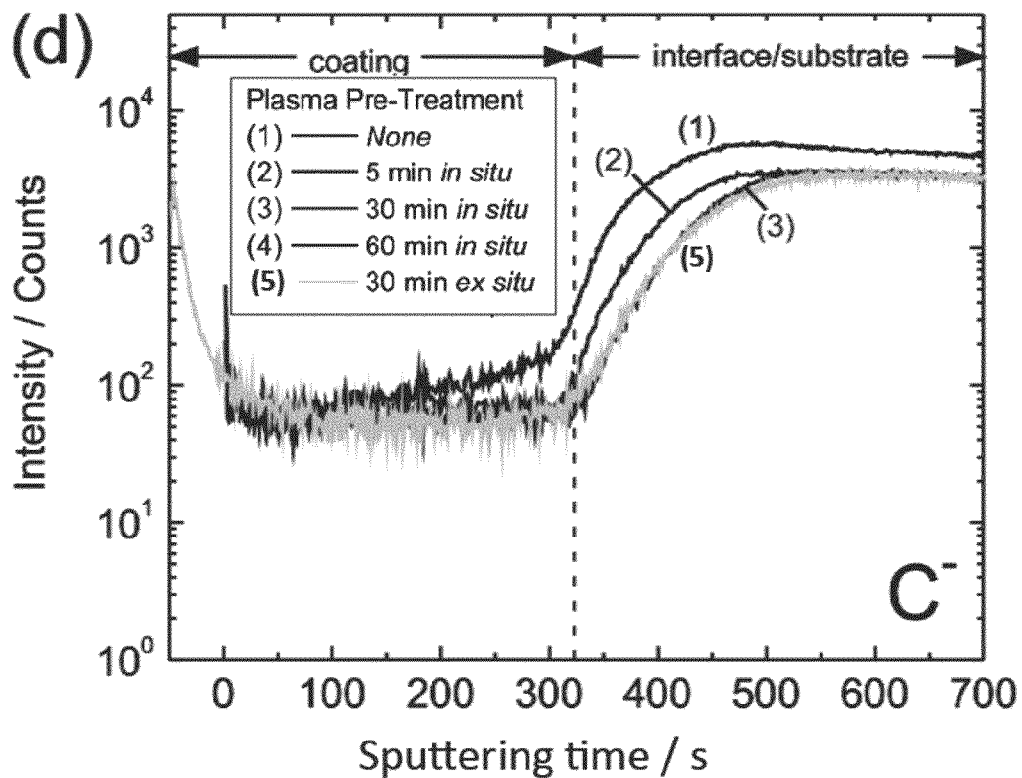
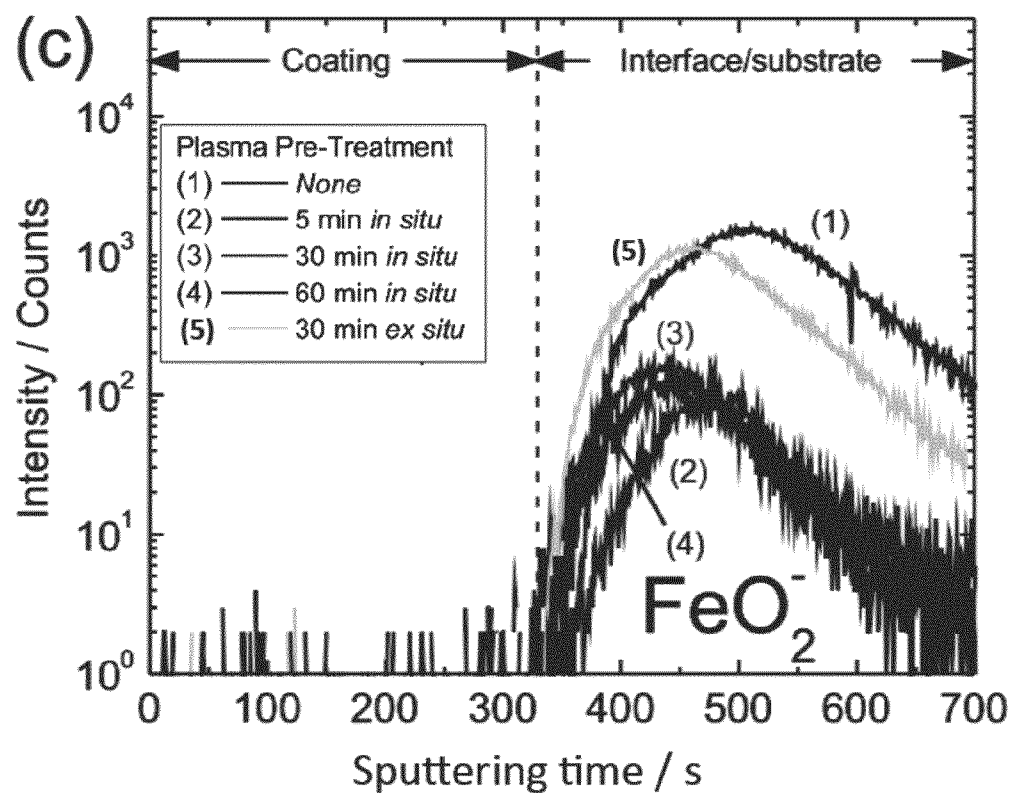
What is claimed:

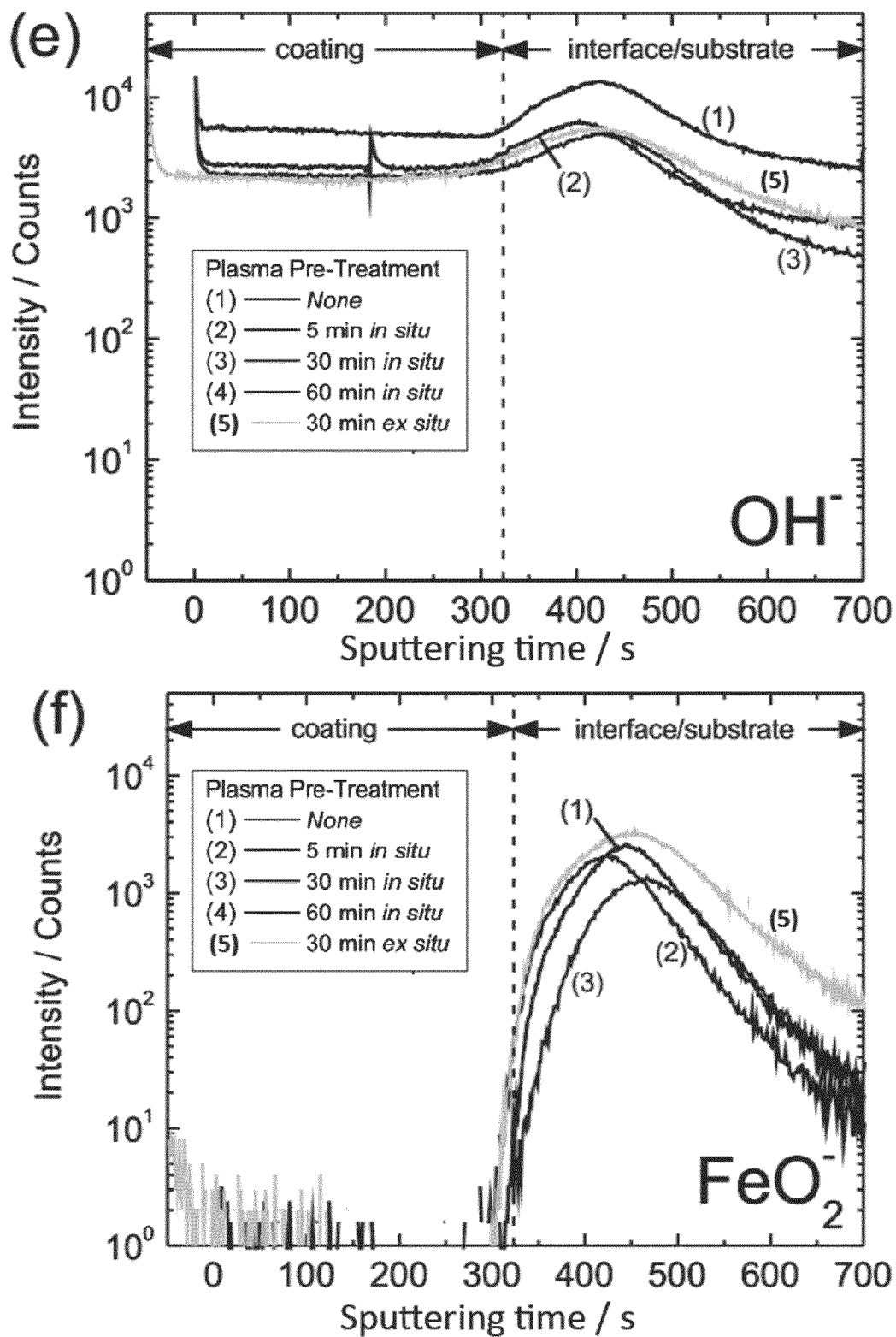
1. A method of improved anti-corrosion properties of thin films, comprising:
 - a. using an argon-hydrogen (Ar-H₂) plasma to pre-treat a substrate; and
 - b. using an atomic layer deposition (ALD) device to deposit a thin film on said substrate, wherein said ALD comprises a thermal ALD or a plasma-enhanced ALD, wherein said ALD comprises a metal, wherein said metal comprises i) s-block element precursor, ii) d-block element precursor, iii) f-block element precursor, or iv) p-block element precursor and an oxygen source.
2. The method of claim 1, wherein said substrate comprises a metal or metal alloy.
3. The method of claim 2, wherein said metal is selected from the group consisting of iron, carbon steel, stainless steel, crucible steel, alloy steel, spring steel, tool steel, aluminum, aluminum alloys, copper, copper alloys, magnesium, magnesium alloys, nickel, nickel alloys, cobalt, cobalt alloys, titanium, zirconium, tantalum, and lead.
4. The method of claim 1, wherein said thin film is selected from the group consisting of metal oxides, metal nitrides, metal carbides, metal carbonates, metal silicides, metal silicates and pure metals.

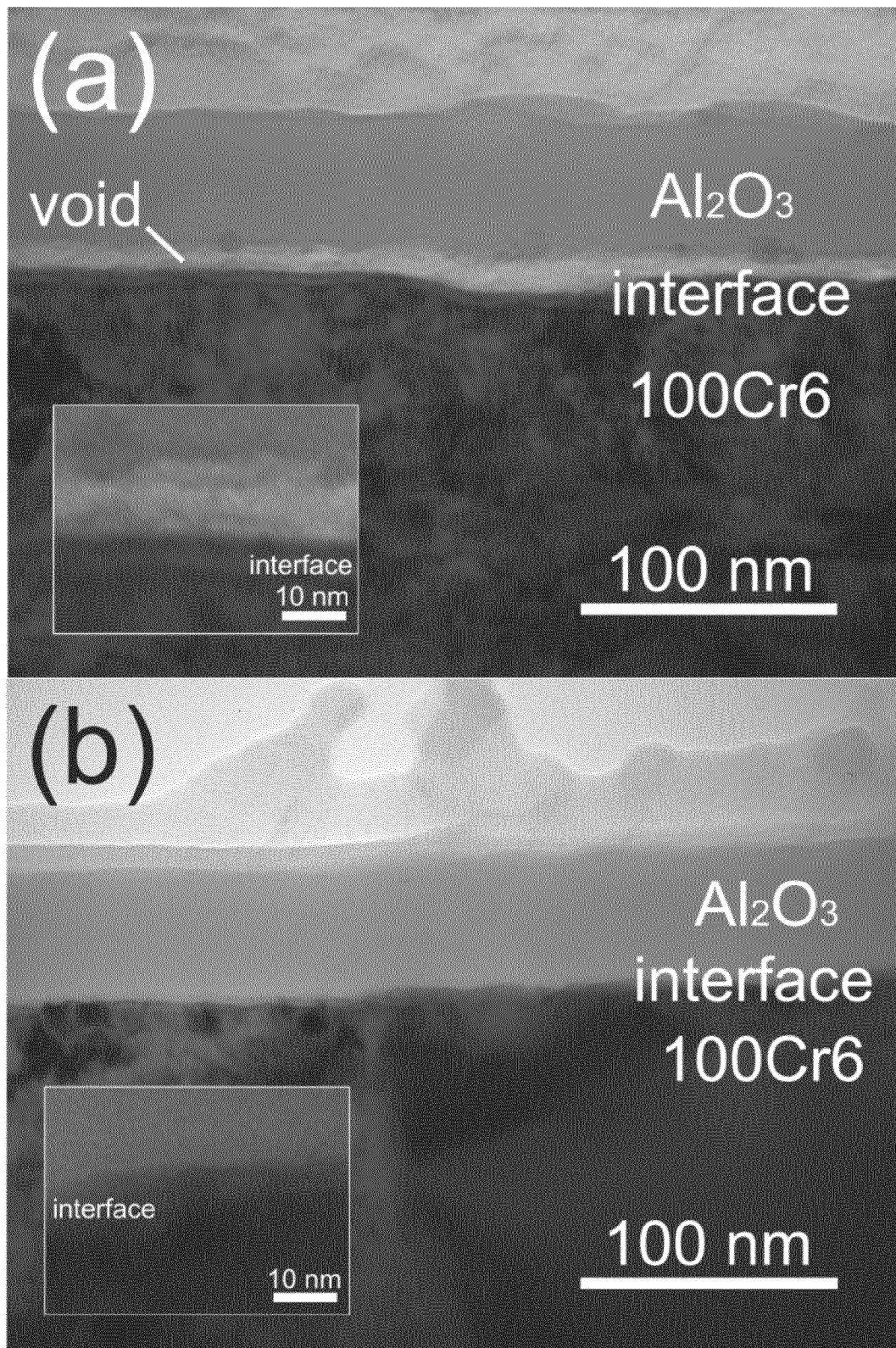
5. The method of claim 4, wherein said film comprises a film stack or a film mixture.
6. The method of claim 1, wherein said argon-hydrogen plasma pre-treatment is applied for a duration in a range of 1 s to 1,000 s.
7. The method of claim 1, wherein said argon-hydrogen plasma pre-treatment comprises a continuous or pulsed plasma.
8. The method of claim 1, wherein said argon-hydrogen plasma pre-treatment comprises an exposure to ambient or no exposure to the ambient.
9. The method of claim 1, wherein said argon-hydrogen plasma pre-treatment comprises either additional treatments or no additional treatments between said plasma pre-treatment and the ALD, wherein said additional treatments are selected from the group consisting of thermal treatment, dry chemical treatments, wet chemical etching, mechanical treatments.

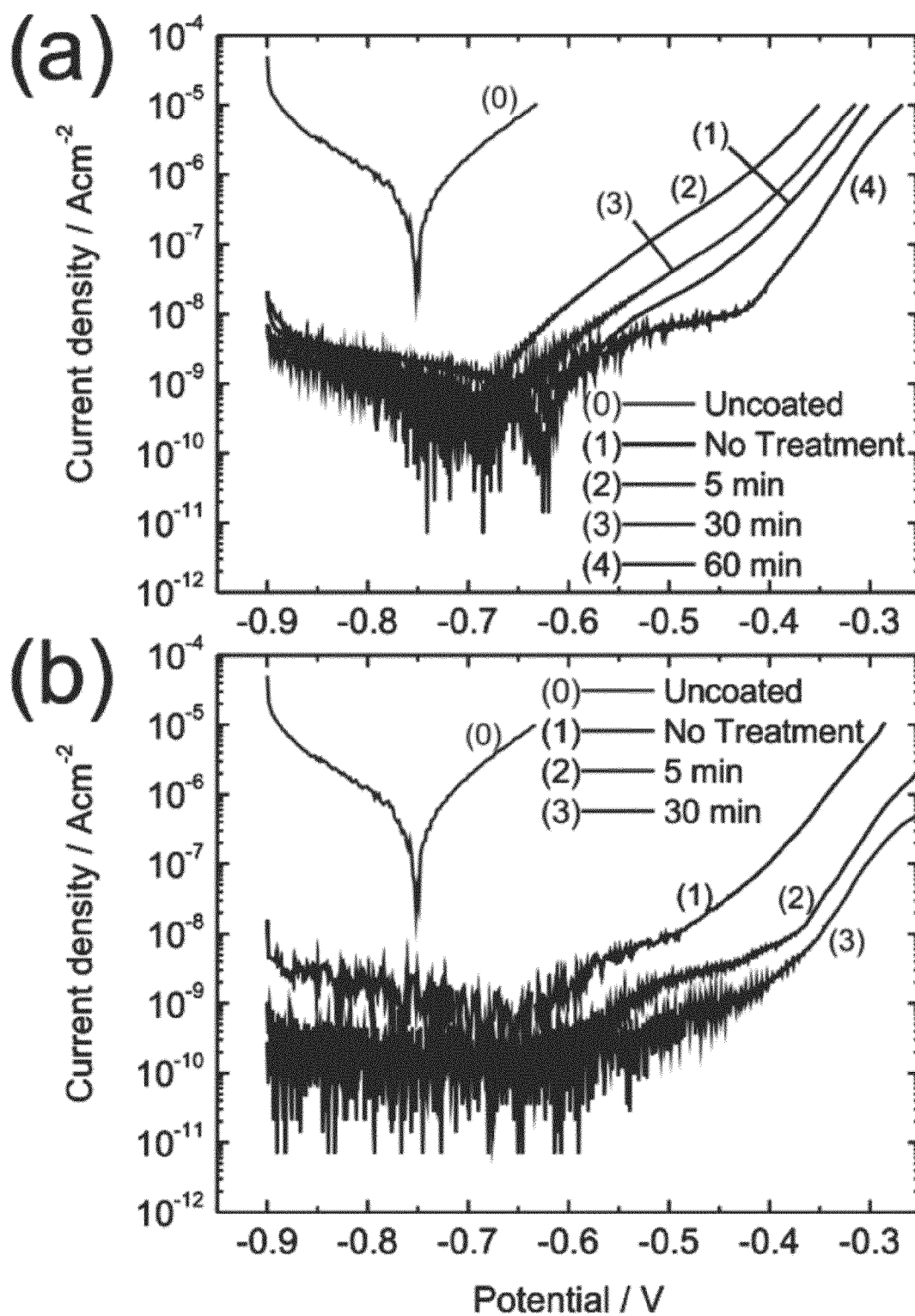
10. The method of claim 9, wherein said mechanical treatments are selected from the group consisting of grinding, lapping, honing and polishing.
11. The method of claim 1, wherein said thin film comprises a thickness in the range of 0.1 nm to 10,000 nm.

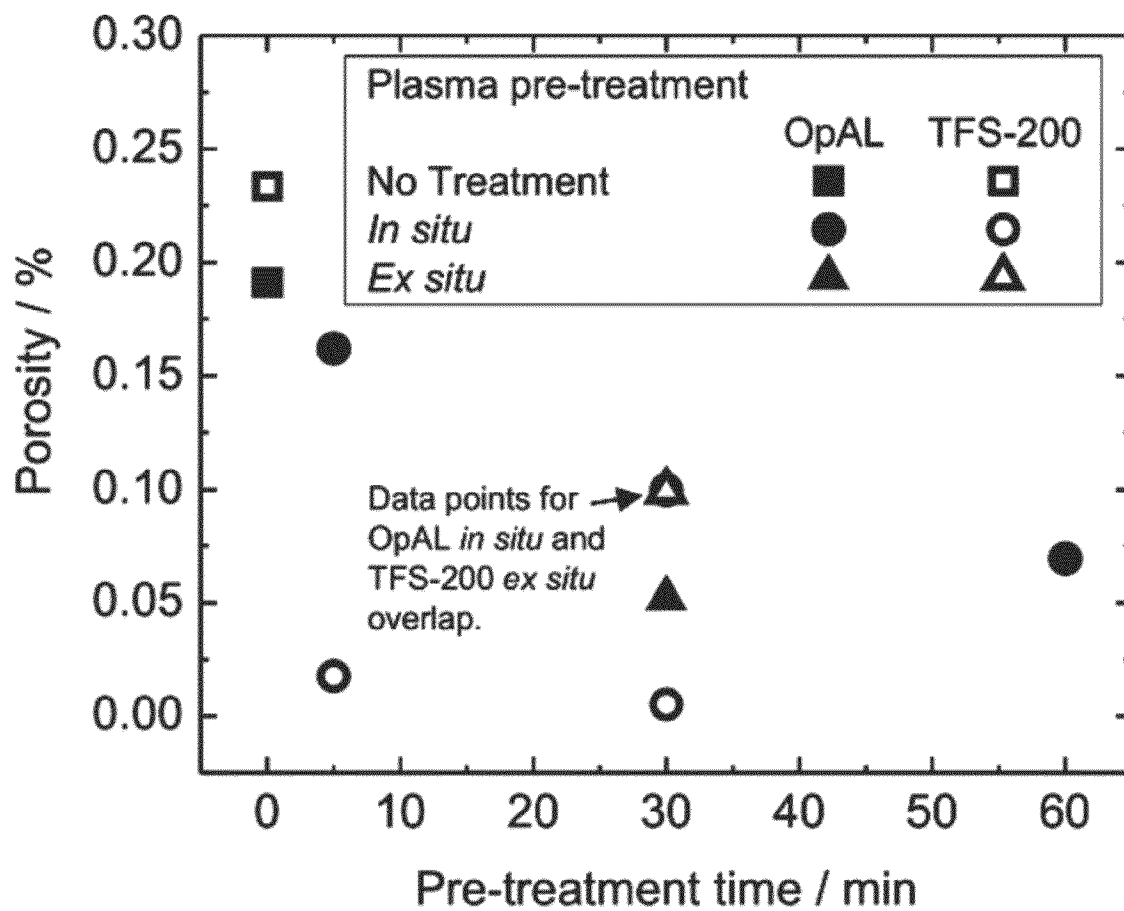
**FIG. 1**

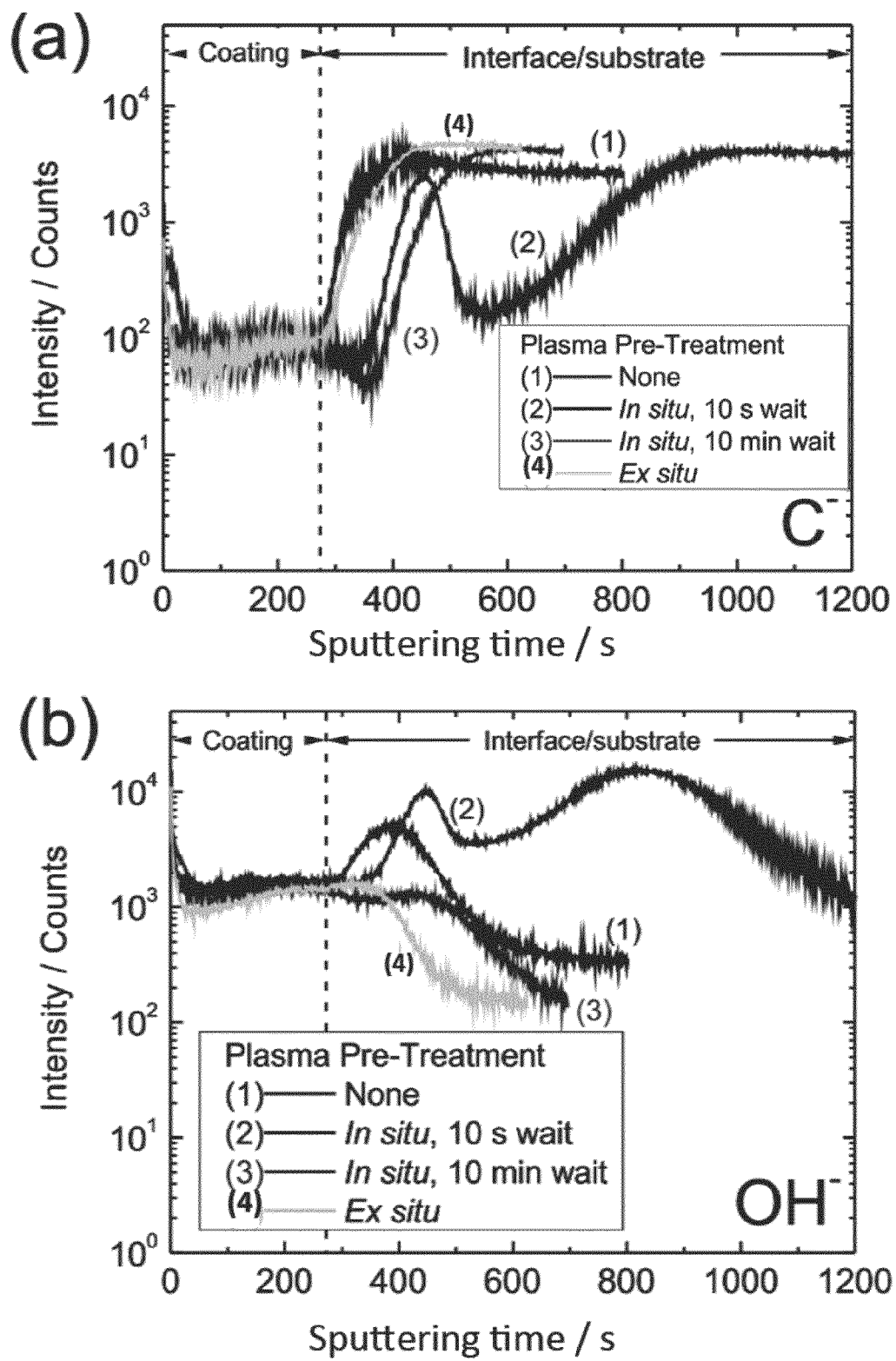
**FIG. 1 (cont.)**

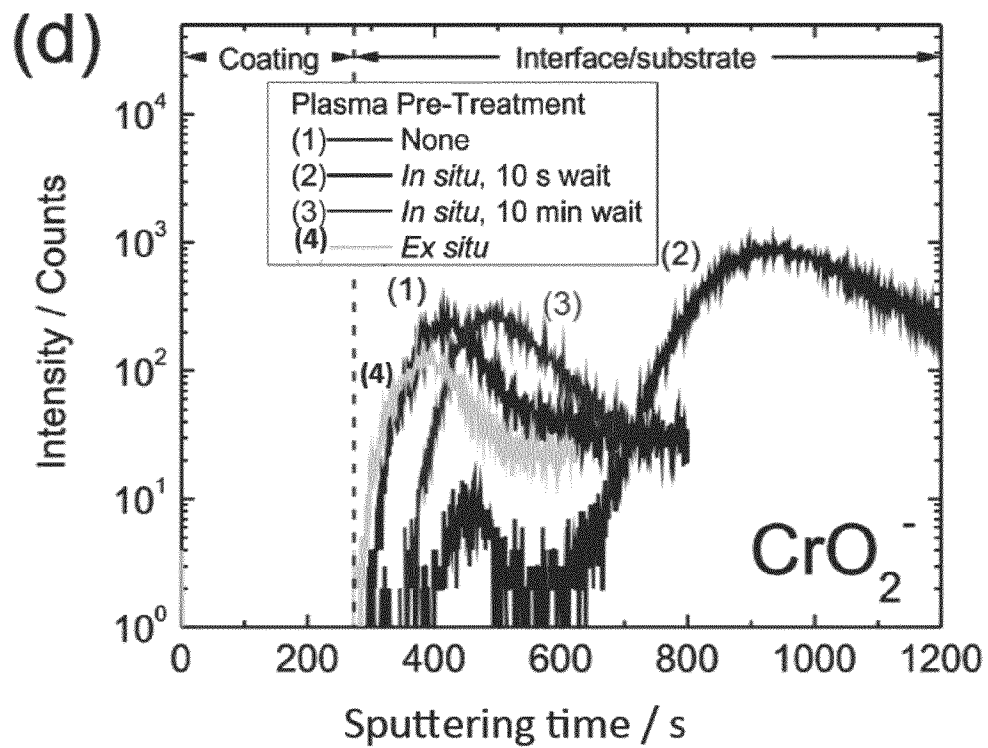
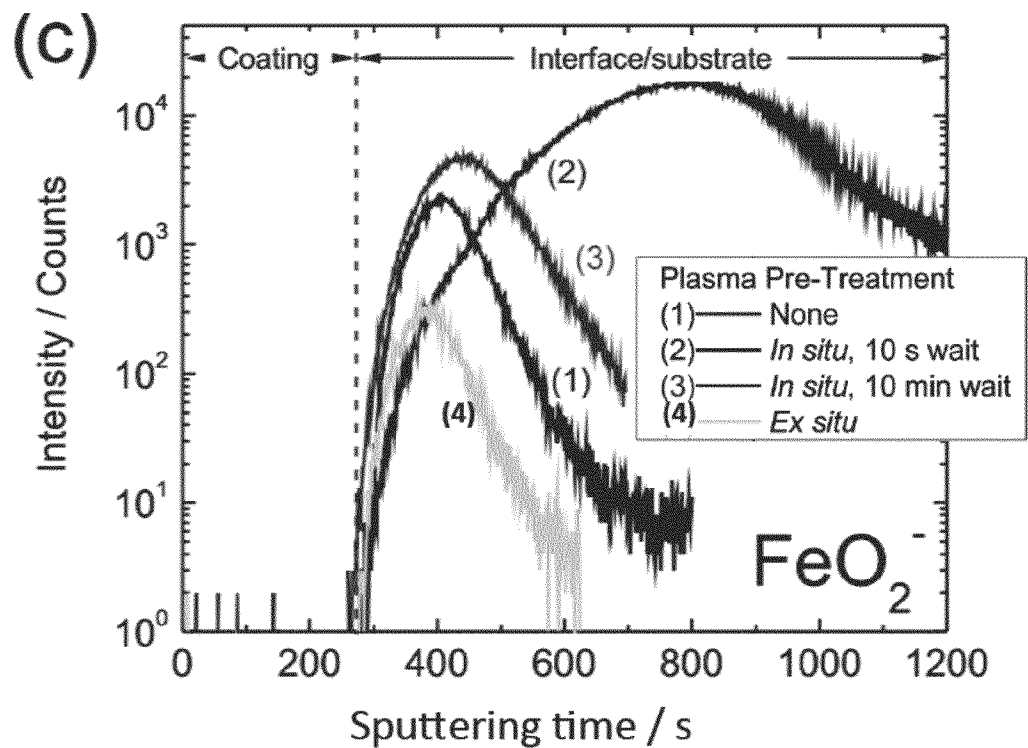
**FIG. 1 (cont.)**

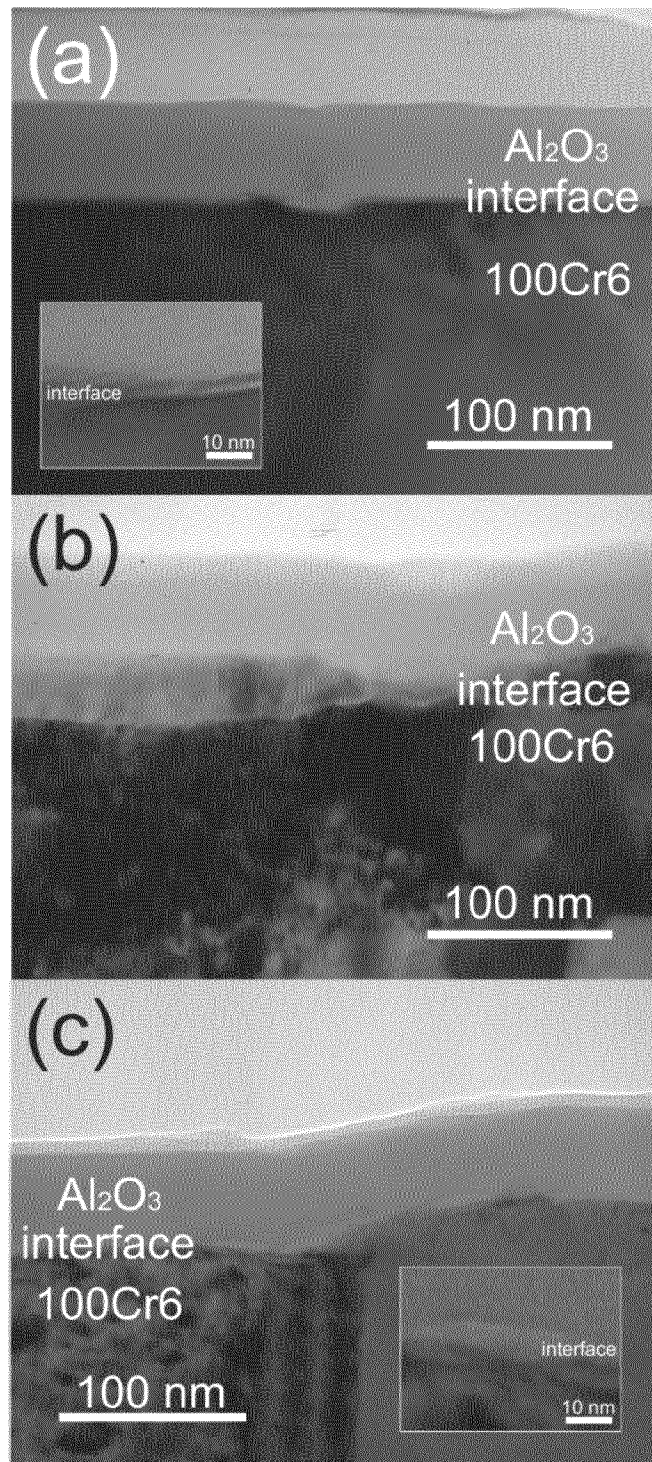
**FIG. 2**

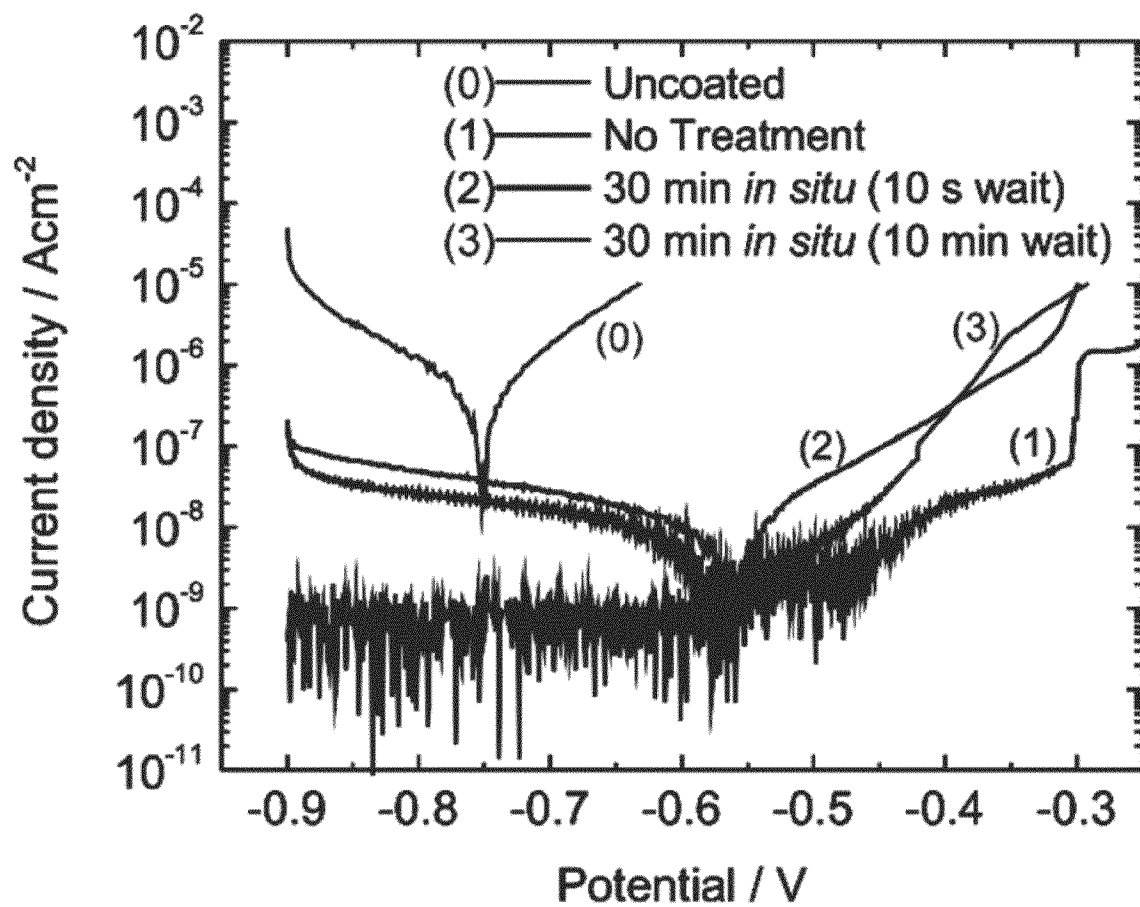
**FIG. 3**

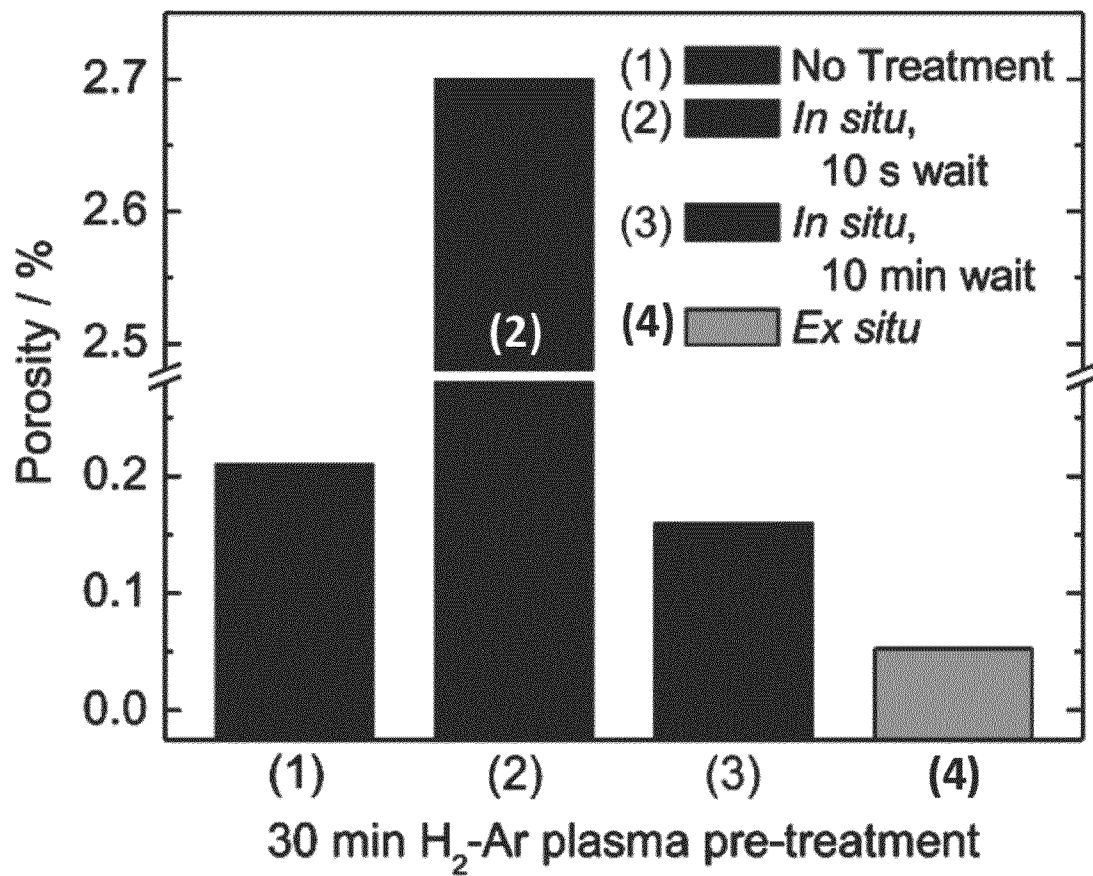
**FIG. 4**

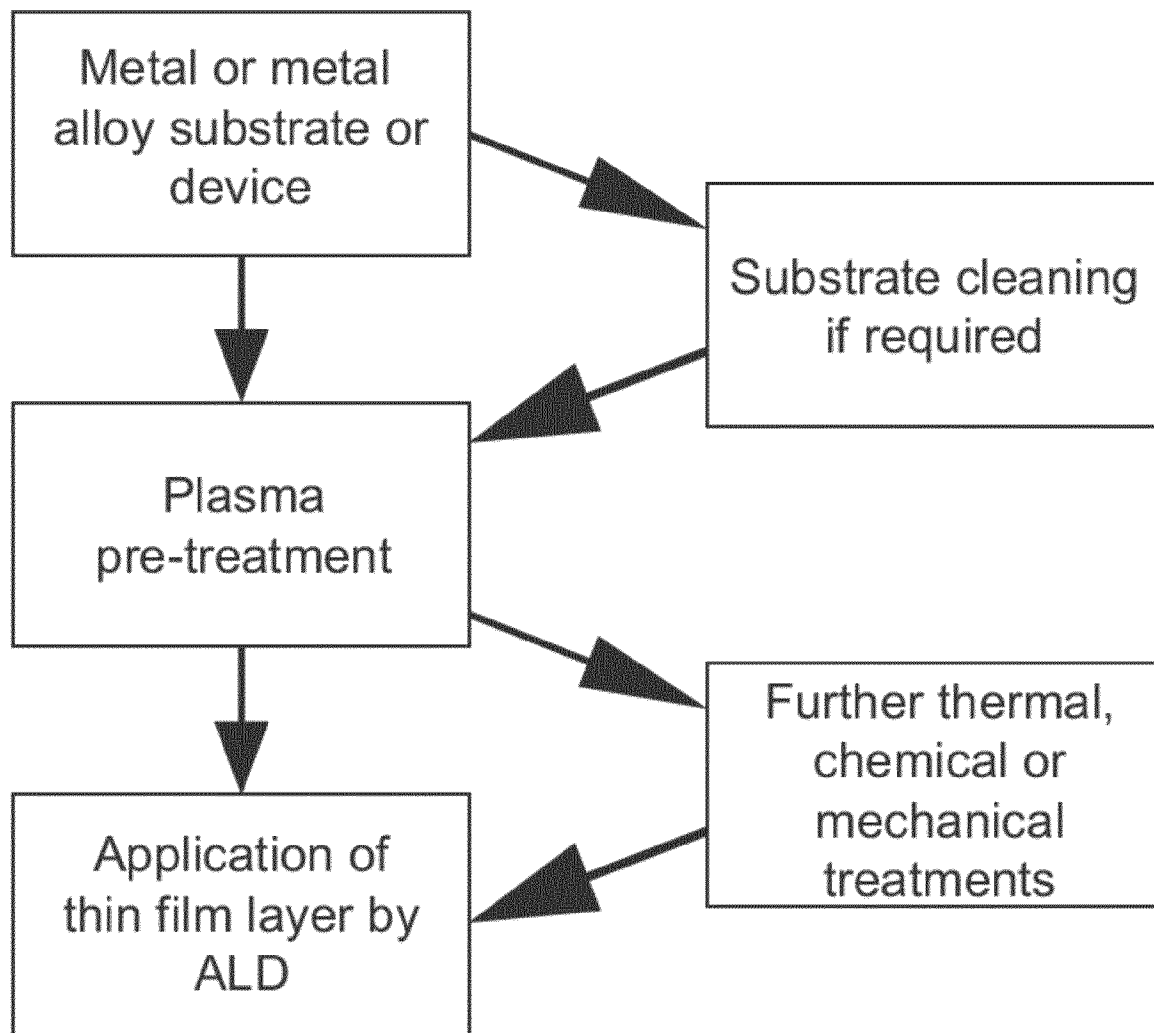
**FIG. 5**

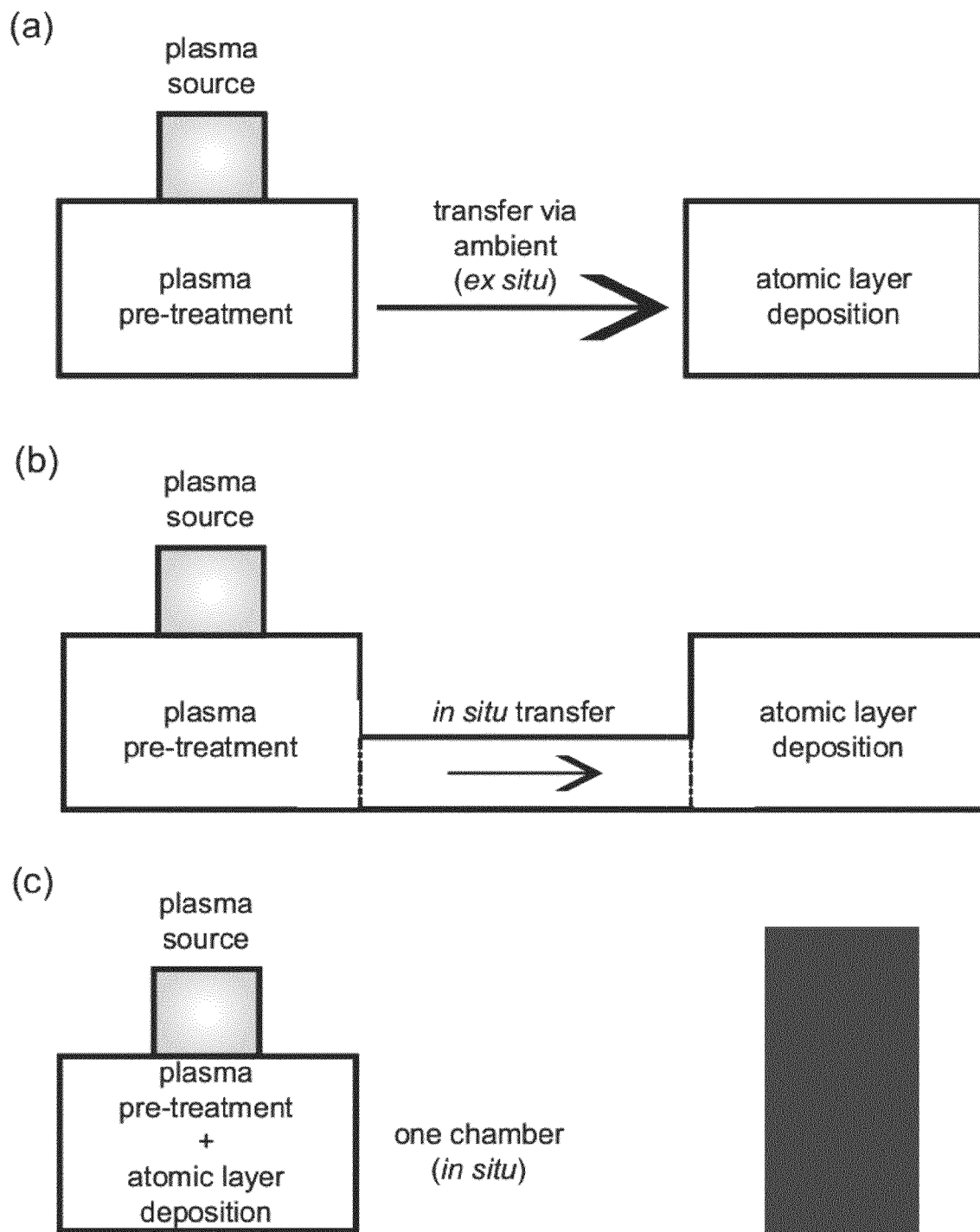
**FIG. 5 (cont.)**

**FIG. 6**

**FIG. 7**

**FIG. 8**

**FIG. 9**

**FIG. 10**

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/060612

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/455
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

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.
Y	EP 2 325 351 A1 (HAFNER GMBH & CO KG C [DE]) 25 May 2011 (2011-05-25) paragraphs [0014] - [0017] -----	1-11
Y	US 2004/043544 A1 (ASAI MASAYUKI [JP] ET AL) 4 March 2004 (2004-03-04) paragraphs [0004], [0091], [0092], [0103] - [0107] -----	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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Date of the actual completion of the international search

29 August 2012

Date of mailing of the international search report

05/09/2012

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/060612

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP 2325351	A1	25-05-2011	DE 102009053889 A1	26-05-2011
			EP 2325351 A1	25-05-2011

US 2004043544	A1	04-03-2004	NONE	
