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

(19) World Intellectual Property Organization
International Bureau

PCT

(43) International Publication Date
17 April 2008 (17.04.2008)

(10) International Publication Number
WO 2008/045226 A1

(51) International Patent Classification:
C23C 16/503 (2006.01) ***C23C 16/40*** (2006.01)

(21) International Application Number: PCT/US2007/021038

(22) International Filing Date: 27 September 2007 (27.09.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/850,225 6 October 2006 (06.10.2006) US

(71) Applicant *(for all designated States except US)*: **DOW GLOBAL TECHNOLOGIES INC.** [US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **RHOTON, Christina, A.** [US/US]; 714 West Saganing Road, Bentley, MI 48613 (US).

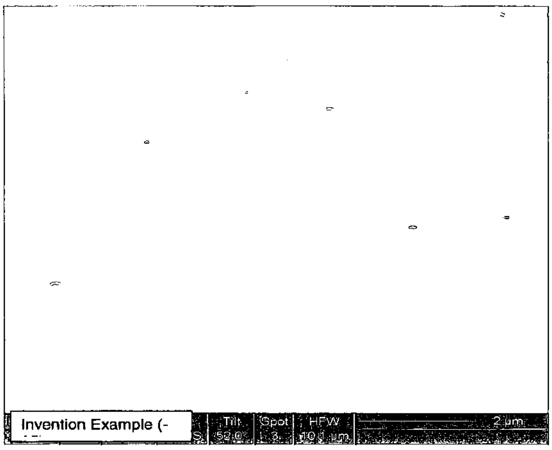
(74) Agent: CHRISTY, M., Robert; The Dow Chemical Company, Intellectual Property, P.o. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, 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, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(54) Title: PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION COATING PROCESS



(57) Abstract: A process for coating or modifying a substrate using plasma-enhanced chemical vapor deposition (PECVD) is described in which a plasma is generated in a gaseous mixture containing at least 35 volume-percent nitrogen gas, at least 50 ppm of at least one gaseous silicon-containing compound, and up to a 1.5: 1 volume ratio of at least one rare gas relative to nitrogen gas, the rare gas comprising at least 1 volume-percent helium gas, at least 1 volume-percent neon gas, or at least 3 volume-percent argon gas, each volume-percent based on the total volume of the gaseous mixture at 200C and 101 kPa pressure. This process is capable of producing coatings which are monolithic and substantially uniform at high deposition rates and/or low power density. The process is useful for making a surface modified coating such as an adhesion promoter or an antifog coating; an optical coating such as a reflective or antireflective coating, a light spectrum management coating, or UV protection coating; a chemical resistant coating; an abrasion-resistant coating; or a gas barrier coating. Examples of potential end use applications include online coating of extruded plastic film, sheet, laminates and molded articles useful in architectural glazing, glazing panels, solar collectors, appliances, optical consumer products and devices, packaging, signage, and transportation.

WO 2008/045226 A1

PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION COATING PROCESS

[0001] This application claims benefit of United States Provisional Application No. 60/850,225, filed October 6, 2006.

Background of the Invention

[0002] The present invention relates to coating or modifying a substrate using plasma-enhanced chemical vapor deposition (PECVD).

[0003] Coating of substrates using PECVD is known. Application of an organosilicon coating via PECVD is described in US-A-5,718,967, WO 03/066932, and US-A-6,815,014. Application of a silicon dioxide coating via PECVD is described in WO 2005/049228. Application of non-silicon metal oxide coatings via PECVD is described in WO2005/113856. The substrates may be plastic materials.

[0004] The state of the art has proposed various solutions to address the problem of how to obtain a commercially acceptable organosilicon or silica coating on various substrates using PECVD at atmospheric pressure.

[0005] However, the state of the art has not yet found a satisfactory method for obtaining coatings having a high degree of smoothness and optical clarity at high coating deposition rates and low cost. In particular, the state of the art has not yet found a solution to the problem of how to reduce costs relating to the consumption of electricity and rare industrial gases such as helium and simultaneously obtain high-quality PECVD coatings.

[0006] These and other problems relating to the process for depositing silicon-containing materials via PECVD are solved by the present invention described below.

Summary of the Invention

[0007] The present invention provides a process for coating or modifying a substrate comprising:

(a) providing a substrate having at least one surface;

(b) providing a gaseous mixture adjacent the at least one surface of the substrate of (a);

(c) generating a plasma in the gaseous mixture of (b), and

(d) allowing the plasma of (c) to form a solid deposit on the at least one surface of the substrate, wherein the gaseous mixture comprises:

at least 35 volume-percent nitrogen gas based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure;

at least 50 ppm of at least one gaseous precursor for forming the solid deposit; and

up to a 1.5:1 volume ratio of at least one rare gas relative to nitrogen gas, the rare gas comprising at least 1 volume-percent helium gas, at least 1 volume-percent neon gas, or at least 3 volume-percent argon gas,

each volume-percent based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

[0008] The present invention also provides a coated or modified substrate obtainable by the above process.

Brief Description of the Drawing

[0010] Fig. 1 is a reproduction of a scanning electron microscope (SEM) image showing the surface morphology of a polycarbonate substrate coated according to Comparative Example 2 described below.

[0011] Fig. 2 is a reproduction of a SEM image showing the surface morphology of a polycarbonate substrate coated according to Comparative Example 1 described below.

[0012] Fig. 3 is a reproduction of a SEM image showing the surface morphology of a polycarbonate substrate coated according to Example 5 of the present invention described below.

Detailed Description of the Invention

[0013] For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques, raw materials, and general knowledge in the art. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight.

[0014] If appearing herein, the term "comprising" and derivatives thereof is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound, unless stated to the contrary. In contrast, the term, "consisting essentially of" if appearing herein, excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term "consisting of", if used, excludes any component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

[0015] As used herein, "nitrogen gas" may be introduced as such or as a component of air.

[0016] As used herein, "oxidizing gas" refers to at least one gas capable of oxidizing at least one precursor.

[0017] As used herein, the term "gaseous precursor" refers to a least one reactive substance in a gaseous state capable of forming a solid deposition on a substrate under PECVD conditions.

[0018] As used herein, the expression, "inert gas" refers to gases which do not react with other components of the gaseous mixture while the gaseous mixture is in the plasma state to form covalently bound compounds with such other components. An "inert gas" does not include oxidative gases or gaseous precursors. Examples include nitrogen gas, argon gas, carbon dioxide gas, neon gas and helium gas.

[0019] Unless otherwise stated herein, the terms "liter" and "cubic centimeter" (cc) refers to the volume of a specified gas, or mixture of gases, at ambient temperature and atmospheric pressure.

[0020] Unless otherwise specified herein, the term "slpm" means "standard liters per minute" and refers to the flow rate of a gas converted to liters per minute at standard temperature and pressure.

[0021] Unless otherwise specified herein, the term "sccm" means "standard cubic centimeters per minute" and refers to the flow rate of a gas converted to cubic centimeters per minute at standard temperature and pressure.

[0022] Unless stated otherwise, the term "volume-percent" refers to the amount of a gas, or mixture of gases, relative to the total volume of the gaseous mixture. As used herein, the volume-percent values and ranges correspond to the partial pressures of the respective gases relative to the total pressure of the gaseous mixture expressed in percent.

[0023] As used herein, ambient temperature refers to a temperature of about 21° C.

[0024] As used herein, standard temperature refers to a temperature of 0° C.

[0025] As used herein, atmospheric pressure refers to a pressure in the atmosphere at ground level, which is generally approximately 101 kPa at sea level.

[0026] As used herein, standard pressure refers to a pressure of 101.3 kPa.

[0027] As defined herein "electrode" refers to a single conductive element or a plurality of conductive elements spaced sufficiently apart within a reactor equipped with sufficient gas flow to form a stable plasma when energized.

[0028] As defined herein, the terms "electrode" and "counter-electrode" are used to refer to a first electrode and a second electrode, either of which can be polarized with the other being oppositely polarized or grounded.

[0029] As defined herein, "frequency" refers to the number of times per second that an applied voltage or electric current cycles from a minimum value to a maximum value and then back again to a minimum value, which may be expressed in Herz (Hz) (i.e., cycles per second).

[0030] As defined herein, "applied voltage" refers to a voltage potential applied to an electrode or counter-electrode.

[0031] The term "metal oxide" refers to compounds containing at least some metal oxygen bonds including polymeric metal oxides containing less than a stoichiometric quantity of oxygen.

[0032] The term "organometal compound" refers to compounds containing both metal and one or more aliphatic, oxoaliphatic, or halogen groups bonded directly to the metal or through one or more oxygen atoms.

[0033] The term "silicon oxide" refers to compounds containing at least some silicon oxygen bonds including polymeric silicon oxides containing less than a stoichiometric quantity of oxygen.

[0034] The term "organosilicon compound" refers to compounds containing both silicon and one or more aliphatic, cycloaliphatic or aromatic groups bonded directly to the silicon or through one or more oxygen or nitrogen atoms.

[0035] It is to be understood by the skilled artisan, that the formulas of the metal oxides, organometal compounds, silicon oxides, and organosilicon compounds prepared herein are empirical formulas and not molecular formulas.

[0036] As used herein the term "monolithic" refers to a solid layer substantially lacking in fissures, cracks and pits. Highly desirably, the solid lacks deformities extending greater than 10 percent of the thickness of the solid layer from the surface. The term "substantially uniform" refers to a solid layer having a mean thickness greater than or equal to 80 percent of the maximum thickness and lacking deformities extending greater than 25 percent of the thickness of the solid layer from the surface.

[0037] The term "highly adherent" or "adhesive layer" refers to a organosilicon film deposited onto an organic polymeric substrate, optionally in combination with a metal oxide surface layer, which multilayer composition does not show loss of anticondensation properties, delamination or loss from the substrate surface when exposed to boiling water at a distance of 10 cm from the surface of the boiling water for at least three minutes, preferably at least 10 minutes. Highly desirably, the organic polymeric substrate comprises a polycarbonate, a polyolefin, or a poly(alkyl)acrylate polymer.

[0038] As used herein, the term "film" with respect to the substrate means any material of any desired length or width and having a thickness from 0.001 up to, but not including, 0.1 cm.

[0039] As used herein, the term "sheet" means a substrate of any desired length or width and having a thickness from 0.1 to 10 cm.

Gaseous Mixture

[0040] The gaseous mixture may be any gaseous mixture as defined above which is capable of forming a deposit on a substrate when subjected to PECVD. The deposit preferably comprises at least one macromolecule, and more preferably at least one polymer. The gaseous mixture comprises nitrogen gas, at least one gaseous precursor, at least one rare gas and, optionally, at least one oxidizing gas.

[0041] The gaseous mixture comprises at least 35, preferably at least 45, more preferably at least 55, even more preferably at least 65, and yet more preferably at least 75, volume-percent nitrogen gas based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

[0042] The volume ratio of the rare gas(es) relative to nitrogen gas is not greater than 1.5:1, preferably not greater than 1:1, more preferably not greater than 1:2, even more preferably not greater than 1:4, and even more preferably not greater than 1:5, based on the gaseous mixture at a temperature of 20°C and 101 kPa.

[0043] The maximum amount of each rare gas is preferably not greater than 37, more preferably not greater than 20, and even more preferably not greater than 10, volume-percent based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

[0044] The amount of helium is preferably at least 1, more preferably at least 2, and even more preferably at least 3, volume-percent, based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

[0045] Alternatively, the amount of neon gas is preferably at least 1, more preferably at least 2, and even more preferably at least 3, volume-percent, based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

[0046] In another alternative, the amount of argon is preferably at least 3, more preferably at least 10, and even more preferably at least 15, volume-percent, based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

[0047] The above amount ranges apply to each of helium, neon, and argon independently (i.e., the amount ranges are satisfied when the amount of only one of helium, neon or argon in the gaseous mixture falls within its respective amount range). In a preferred embodiment, helium is present in the gaseous mixture in an amount within one or more of the above preferred amount ranges for helium.

[0048] Examples of optional suitable oxidizing gases include oxygen, nitrous oxide (N_2O), ozone (O_3), nitric oxide (NO), and nitrogen tetraoxide (N_2O_4), as well as combinations thereof. Oxygen may be introduced as such or as a component of air.

[0049] When a macromolecular or polymeric deposit is desired, the oxidizing gas is preferably present in the gaseous mixture in an amount of at least 1 volume-percent, more preferably at least 5, more preferably at least 10, and even more preferably at least 15, volume-percent based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure. The ratio of precursor to oxidizing gas is preferably at least 2.5×10^{-4}, and more preferably at least 1.25×10^{-3}, up to 0.05, and more preferably up to 0.03.

[0050] The oxidizing gas may be absent or present in the gaseous mixture at a low concentration, such as less than 1, more preferably less than 0.1, even more preferably less than 0.01, volume-percent, based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure, and even more desirably a substantial absence of an oxidizing gas, to obtain a substrate having an adhesive coating as described, for example, in WO 2006/036461 and WO 2006/049794.

[0051] The process according to this invention may be used to make a substrate having a multi-layer coating comprising at least one macromolecular or polymeric layer and at least one adhesive layer as described in WO 2006/036461.

[0052] The process according to this invention may be used to make a substrate having a coating comprising at least one metal oxide layer as described in WO 2005/113856, for example.

[0053] The rate ratio of oxidizing gas(es) to inert gases is preferably in the range from 0 to 3:10. Preferred rate ratio sub-ranges include a minimum of 1:50 and 1:10 and maximum ratios of 1:10 and 1:50. The preferred ranges and sub-ranges include all possible combinations of the aforementioned lower and upper endpoints.

[0054] The gaseous precursor may or may not be gaseous at ambient temperature and atmospheric pressure. When the gaseous precursor is not gaseous at ambient temperature and atmospheric pressure, the precursor may be evaporated by the application of heat, agitation, electron discharge, microwave energy and/or vacuum in order to combine the precursor with the inert gas(es) and any oxidizing gas(es). A well-known device which may be used to evaporate one or more nongaseous precursors to form the gaseous precursor and combine it with the other gases is a controlled evaporator mixer.

[0055] In a preferred embodiment, at least one precursor is mixed with helium gas prior to adding the precursor to the other components of the gaseous mixture. In one embodiment, the precursor is added by sweeping the helium gas over the precursor while the precursor is undergoing agitation or heating.

[0056] The precursor is preferably capable of forming at least one macromolecule and/or at least one polymer when subjected to PECVD. When the gaseous precursor is a silicon-containing compound, the precursor is preferably capable of forming an organosilicon or silicon oxide deposition under PECVD conditions. When the gaseous precursor is at least one metal-containing compound, the precursor is preferably capable of forming a metal oxide deposition under PECVD conditions.

[0057] Examples of suitable precursors for making an organosilicon or silicon oxide deposit include silicon-containing compounds such as silanes, siloxanes, and silazanes. Preferred silicon-containing compounds may be represented by the chemical formula (I):

$$R_3Si[X\text{-}Si(R')_2]_rR'' \qquad (I)$$

wherein R, R', and R", independently at each occurrence, represent -H, -OH, a C_{1-10} hydrocarbyl group, or a C_{1-10} hydrocarbyloxy group, X represents –O- or –N(R"")-, wherein R'''', independently at each occurrence, represents –H or a C_{1-10} hydrocarbyl group, and r represents zero or a number in the range from 1 to 10. The hydrocarbyl and hydrocarbyloxy groups may be saturated or unsaturated, substituted or unsubstituted, and branched or unbranched. The silicon-containing compounds are preferably organosilicon compounds and preferably comprise at least one, more preferably at least three, C_{1-10} hydrocarbyl group(s) and/or at least one, preferably at least three, C_{1-10} hydrocarbyloxy group(s). Each of the C_{1-10} hydrocarbyl groups and C_{1-10} hydrocarbyloxy groups preferably comprise up to three carbon atoms.

[0058] Examples of silanes include dimethoxydimethylsilane, methyltrimethoxysilane, tetramethoxysilane, methyltriethoxysilane, diethoxydimethylsilane, methyltriethoxysilane, triethoxyvinylsilane, tetraethoxysilane (also known as tetraethylorthosilicate or TEOS), dimethoxymethylphenylsilane, phenyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-methacrylpropyltrimethoxysilane, diethoxymethylphenylsilane, tris(2-methoxyethoxy)vinylsilane, phenyltriethoxysilane, and dimethoxydiphenylilane.

[0059] Examples of siloxanes include tetramethyldisiloxane (TMDSO), hexamethyldisiloxane (HMDSO), and octamethyltrisiloxane.

[0060] Examples of silazanes include hexamethylsilazanes and tetramethylsilazanes.

[0061] These precursors may be used to make deposits or coatings comprising polymeric organosilicon, polymeric siloxane, and/or silicon oxide depending on the starting material and the amount of oxidizing gas present. The presence of a low or zero concentration of oxidizing gas may be used to produce polymeric organosilicon deposits or coatings, particularly when the precursor comprises silanes or silazanes. Increasing the concentration of the oxidizing gas may be used to promote the production of a polysiloxane or silicon oxide deposit or coating.

[0062] Examples of suitable precursors for making metal oxide deposits include metal-containing compounds such as alkyl, alkoxy, or halo zincs, tins, aluminums, and titaniums. Preferred metal-containing compounds may be represented by the chemical formula (II):

$$MR_aX_b \qquad (II)$$

wherein M is a metal represented by Zn, Sn, Al, and Ti; R, independently at each occurrence, represents -H, -OH, a C_{1-10} hydrocarbyl group, or a C_{1-10} hydrocarbyloxy group, X represents a halogen including Cl or Br; and "a" and "b" each represent whole numbers of R and X moieties, previously described, in the range from zero to the valence of M, provided that the total of a + b equals the valence of the metal M; or a volatile salt thereof.

[0063] Examples of suitable metal-oxide precursors include diethyl zinc, dimethyl zinc, zinc acetate, titanium tetrachloride, dimethyltin diacetate, zinc acetylacetonate, zirconium hexafluoroacetylacetonate, zinc carbamate, trimethyl indium, triethyl indium, cerium (IV) (2,2,6,6-tetramethyl-3,5-heptanedionate), and mixtures thereof.

[0064] Examples of metal oxides include oxides of zinc, tin, titanium, indium, cerium, and zirconium, and mixtures thereof.

[0065] Desirably, the concentration of precursor present in the gaseous mixture is maintained in the range from at least 50 ppm, preferably at least 200 ppm, and more preferably at least 500 ppm, to not greater than 10000 ppm, preferably not greater than 8000 ppm, and more preferably not greater than 7000 ppm.

[0066] In a preferred embodiment, the gaseous mixture is a mixture of precursor with air in which the concentration of precursor compound is preferably within one or more of the above-stated precursor concentration ranges.

[0067] The flow rate and concentration is preferably adjusted to obtain an average thickness of the coating on the substrate not greater than 5 μm, more preferably not greater than 2 μm, even more preferably not greater than 1 μm, and even more preferably not greater than 0.1 μm and preferably at least 1 nm, more preferably at least 10 nm, and even more preferably at least 30 nm, and a variation in thickness relative to the average thickness not greater than 1 μm, more preferably not greater than 0.5 μm, and even more preferably not greater than 0.1 μm. The variation in thickness relative to the average thickness is preferably not greater than 50 percent, more preferably not greater than 20 percent, and even more preferably not greater than 10 percent.

[0068] Preferably the velocity of the gaseous mixture is such that a stable plasma is formed allowing for uniform deposition of polymerized product. Desirably, the velocity of the gaseous mixture passing over the substrate is at least about 0.05 m/s, more preferably at least about 0.1 m/s, and most preferably at least about 0.2 m/s; and preferably not greater than about 1000 m/s, more preferably not greater than about 500 m/s, and most preferably not greater than about 200 m/s. Preferably, the volumetric flow of the gaseous mixture is from 10 to 1,500 cc/minute per cm^2 of the surface area exposed to a plasma-generating energy.

[0069] The gaseous mixture introduced in step (b) preferably has a pressure of about 101 kPa +/- 20 kPa, such as at about atmospheric pressure, and a temperature of about 20°C +/- 30°C, such as at ambient temperature.

[0070] The gaseous mixture is preferably introduced in step (b) at a pressure in the range from 1 Pa to 800 kPa above atmospheric pressure. The gaseous mixture is preferably introduced at a pressure sufficiently above atmospheric pressure to obtain the desired gas flow past the electrode(s).

Substrate

[0071] The substrate used in the present invention is not limited. Examples of substrates include glass, metal, ceramic, paper, fabric, and plastics such as polyolefins including polyethylene and polypropylene, polystyrenes, polycarbonates, and polyesters including polyethylene terephthalate and polybutylene terephthalate.

[0072] In a preferred embodiment, the substrate used in the present invention includes organic polymers in any form. Examples of substrates include films, sheets, fibers, and woven or non-woven fabrics of thermoplastics, such as polyolefins including polyethylene, polypropylene, and copolymerized mixtures of ethylene, propylene, and/or a C_{4-8} α-olefin, polystyrenes, polycarbonates, polyesters including polyethylene terephthalate, polylactic acid, and polybutylene terephthalate, polyacrylates, polymethacrylates, and interpolymers of any of the monomers employed in the foregoing polymers.

[0073] The organic polymeric substrate of the present invention may comprise one or more layers and has a first and a second surface. In the process of the present invention, the first and/or second surface of the organic polymeric substrate can be coated. The coated substrate is referred to herein as a composite. A preferred substrate is polycarbonate.

[0074] It is to be understood, that the foregoing structures may comprise a laminate of one or more layers of the same or different organic polymer, and include as well any other suitable material, such as wood, paper, metal, cloth, or oxides of one or more metal or metalloids, exemplified by clay, talc, silica, alumina, silicon nitride, or stone, as one or more layers of a multilayer structure or as a component of one or more layers, with the proviso that the exposed surface of the substrate comprise one or more organic polymers. Laminates may be made by any process known in the art, for example, but not limited to, coextrusion, lamination by heat, lamination using an adhesive, and the like. A preferred laminate comprises a polycarbonate sheet and a polycarbonate film wherein the polycarbonate comprising the film contains a UV absorber. Another preferred laminate is a polycarbonate sheet having a first and a second surface wherein a polycarbonate film comprising UV absorbers is laminated to the first and second surface of the polycarbonate sheet; said polycarbonate films may have the same or different compositions. Alternatively, the film comprising the UV absorber is preferably a poly(meth)acrylate. In one embodiment, the UV absorber is grafted, copolymerized, or otherwise bound to the organic polymer.

Plasma Generation

[0075] Any suitable apparatus may be used to generate a plasma in step (c). Examples include those devices previously disclosed in US 5,433,786, WO 2003/066932, WO 2003/066933, WO 2005/049228, Ward et al., Langmuir, 2003 19, 2110-2114, and elsewhere. In all of the foregoing apparatuses, the precursor is supplied as a vapor to a flowing stream of a gas (carrier gas) in the vicinity of an electrode, preferably by passing through or over the surface of the electrode, where a plasma is produced between the electrode and a counter-electrode. The amount of precursor may be increased by use of heating to increase the vapor pressure thereof or by atomization using, for example, an ultrasonic atomizer. The latter method for achieving sufficient vapor pressure of the precursor is preferred due to the avoidance of elevated temperatures that may approach the auto-ignition temperature of the gaseous mixture. Although the process is referred to as operating at atmospheric pressure, it is to be understood that pressures slightly above or below atmospheric (± 20 kPa) are operable as well. Preferably the operating pressure is atmospheric or sufficiently above atmospheric pressure as needed to obtain the desired gas flow past the electrode(s).

[0076] The above examples of suitable apparatus include apparatus for generating a plasma via plasma discharge such as a dielectric barrier discharge apparatus. Such devices comprise one or more electrodes and one or more counter-electrodes and the ability to apply a voltage potential between the electrode(s) and the counter-electrodes. A plasma is produced by electrical discharge between the electrode(s) and the counter-electrode(s).

[0077] Dielectric barrier discharge is also known as "silent" and "atmospheric-pressure-glow" discharge. The application of dielectric barrier discharge for making an organosilicon coating via PECVD is described in US-A-5,718,967, WO 03/066932, and US-A-6,815,014. The application dielectric barrier discharge for making a silicon dioxide coating via PECVD is described in WO 2005/049228. The application dielectric barrier discharge for making a metal oxide coating via PECVD is described in WO 2005/113856.

[0078] In the process of the present invention, sufficient electric power density and frequency are applied to an electrode and/or counter-electrode to create and maintain a glow discharge in the gaseous mixture located in a gap between the electrode and counter-electrode. The power density (based on electrode surface area exposed to the plasma) is preferably at least 0.5 W/cm^2, more preferably at least 1 W/cm^2, and most preferably at least 9 W/cm^2; and preferably not greater than 370 W/cm^2, more preferably not greater than 140 W/cm^2, and most preferably not greater than 40 W/cm^2. The current applied to the electrodes may vary from 10 to 10,000 watts, preferably from 100 to 1000 watts, at potentials of 10 to 50,000 volts, preferably 100 to 20,000 volts. The frequency is preferably at least 2 kHz, more preferably at least 5 kHz, and most preferably at least 10 kHz; and preferably not greater than 100 kHz, more preferably not greater than 60 kHz, and most preferably not greater than 40 kHz.

[0079] To obtain efficient conversion of electric power into plasma, the frequency is preferably selected to coincide with the resonance frequency of the electrode(s)/counter-electrode(s) configuration. The resonance frequency is equal to the inverse of $2\pi \sqrt{(L \bullet C)}$ in which L is the inductance, provided almost entirely by the high-voltage side of the transformers, and C is the capacitance provided almost entirely by the electrode-to-ground arrangement at the coating station. The inductance is preferably provided primarily by the high-voltage side of an electrical transformer and the capacitance is preferably provided primarily by a counter-electrode-to-ground arrangement.

[0080] In a preferred embodiment, electric power is applied to the electrode(s) and the counter-electrode(s) are grounded (i.e., connected to the earth via an electric conductor). In this embodiment, the voltage applied to the electrode(s) preferably cycles between a minimum voltage value and a maximum voltage value at a substantially constant frequency. The maximum voltage value is preferably either a positive value or a negative value in each cycle in contrast to cycles in which the maximum voltage alternates between a positive value and a negative value.

[0081] The spacing between electrode and counter-electrode is preferably sufficient to achieve and sustain a visible plasma (glow discharge), preferably at least 0.1 mm, more preferably at least 1 mm, and preferably not more than 50 mm, more preferably not more than 20 mm, and most preferably not more than 10 mm. The electrode, the counter electrode or both the electrode and the counter-electrode may be fitted with a dielectric sleeve, if desired. In one embodiment, the electrode and counter electrode pair are encased within a high temperature resistant dielectric, such as a ceramic.

[0082] The substrate to be coated may be supported or transported by the counter-electrode or otherwise supported in the vicinity of the plasma in order to be contacted or impinged by at least a portion of the plasma generated by the electrode and counter-electrode. The flow of the gaseous mixture together with the plasma generated in the vicinity of the electrodes causes plasma polymerized product to be deposited onto the surface of the substrate attached to the counter-electrode or placed in the vicinity of an electrode pair. A suitable gap is provided between the substrate and the electrode or electrodes for exhaust of the carrier gas, by-products and unattached products. The width of the gap is adjusted to prevent incursion of excess amounts of contaminating gases. The electrode(s) and the counter-electrode(s) are preferably located within 4 mm, more preferably within 1 mm of the surface of the substrate.

[0083] Any suitable electrode geometry and reactor design can be employed in the present process. For thick substrates, such as sheet material, it may be desirable that both the electrode and the counter-electrode be located on the same side of the substrate to be coated. Plasma created reaction products are impinged onto the surface of the substrate after passing by the electrodes. Exhaust ports from the reactor are located near the substrate surface and spatially removed from the electrodes to permit contact of the plasma or at least the reaction products formed therein with the substrate surface before exiting the reactor. If desired, the shape of the resulting corona discharge may be modified by the use of a magnetic field as previously disclosed in the art. For thinner substrates, the counter electrode may be a conductive surface upon which the target or substrate is supported. Either the substrate or the entire counter-electrode containing the substrate may be moving, especially in a continuous treating process.

[0084] Plasma generation is preferably applied to the substrate as the substrate and the plasma-generating apparatus are displaced relative to one another over time. In one embodiment, the substrate is displaced relative to a stationary plasma-generating apparatus over time during step (c). The movement of the substrate relative to the plasma-generating apparatus is preferably at least 20 cm, more preferably at least 50 cm, per minute and preferable up to 8 m, more preferably up to 3 m, per minute.

[0085] The process according to the present invention is capable of depositing a coating at high deposition rates. In a preferred embodiment of this invention, a coating is deposited at a rate of at least 0.008, more preferably at least 0.06, and even more preferably at least 0.2, mg / (cm.^{2} * minute).

[0086] The process according to the present invention is capable of depositing a coating at an improved electric power use efficiency relative to using either air or a rare gas as the carrier gas or balance gas.

[0087] Plasma polymerization as carried out by the process of the present invention preferably results in an optically clear coating deposited on the substrate. The term "optically clear" is used herein to describe a coating having an optical clarity of at least 70 percent, more preferably at least 90 percent, and most preferably at least 98 percent and a haze value of preferably not greater than 10 percent, more preferably not greater than 2 percent, and most preferably not greater than 1 percent. Optical clarity is the ratio of transmitted-unscattered light to the sum of transmitted-unscattered and transmitted-scattered light (<2.5°). Haze is the ratio of transmitted-scattered light (>2.5°) to total transmitted light. These values are determined according to ASTM D 1003-97.

[0088] The process according to the present invention is capable of producing coatings which are monolithic and substantially uniform at higher deposition rates and/or lower power density than prior processes.

<u>Examples</u>

[0089] The invention is further illustrated by the following examples that should not be regarded as limiting of the present invention. Unless stated to the contrary or conventional in the art, all parts and percents are based on weight.

Test Protocol

[0090] A polycarbonate substrate having a width of 10 cm. and a thickness of 0.25 inch (0.635 cm.) is placed on a conveyer belt passing through an APC 2000 atmospheric plasma coater (available from Sigma Technologies of Tucson, Arizona, U.S.A.) fitted with Generation 2.4 electrodes (also available from Sigma Technologies) at a rate of 2 meters/minute. The electrodes are dimensioned to apply energy to a 54 cm^2 area over the full width of the substrate as the substrate passes through the plasma coater.

[0091] The gaseous mixture used in each example comprises 250 sccm helium sweeps over TMDSO. Nitrogen gas and oxygen gas, as an oxidizing gas, are provided in Comparative Example 1 and Examples 1 to 4 of the present invention by introducing air as a gaseous mixture component. The average linear gas velocity of the gaseous mixture in

Comparative Example 1 and Examples 1 to 4 is 300 ft./min. (91.4 m/min.). The average linear gas velocity of the gaseous mixture of Comparative Example 2 is 80 ft./min. (24.4 m/min.).

[0092] Each gas mixture is introduced above the substrate using a drilled hole gas delivery tube. While the gas mixture is passing through the electrodes and occupying the space between the electrodes and the substrate, 2 kW electric power is applied to the electrodes for a time period of 1 minute while the substrate passes through the plasma coater, so that 2 meters of substrate per example are subjected to plasma-enhanced chemical vapor deposition at a power density of 37 W/cm^2.

[0093] Film thickness measurements are conducted using a Filmetrics F20 film thickness measuring device together with FILMeasure™ software, both available from Filmetrics, Inc., of San Diego, California, U.S.A.

[0094] The test data and results are summarized below.

Test Data and Results

[0095] Data obtained using the above test protocol is shown in Table 1 below.

Table 1

TEST RESULTS

EXAMPLE DESIGNATION	AIR (SLPM)	HELIUM (SLPM)	HE / N_2 VOL. RATIO	VOL. % HE	THICKNESS (MICRONS)
COMPAR. EX. 1	84	0.25	0.004	0.3	0.2
COMPAR. EX. 2	0	15.25	NA	100	NM (1)
1	84	2.25	0.03	2.3	0.43
2	84	5.25	0.08	5.9	0.42
3	84	10.25	0.16	10.9	0.43
4	84	15.25	0.23	15.4	0.41

(1) Thickness of the deposition according to Comparative Example 2 was not measured (NM), because the deposition was too rough and powdery and, therefore, not satisfactory as shown in Fig. 1.

[0096] As can be seen from the data in Table 1, the addition of helium at a concentrations in the range from 2.3 to 15.4 volume-percent results in a coating thickness at least twice that of Comparative Example 1 conducted without helium.

[0097] Comparative Example 2 conducted with helium, but in the absence of air, provides an unsatisfactory powdery coating as shown in the SEM image of Fig. 1.

[0098] The SEM image of Fig. 2 shows that Comparative Example 1 provides a smoother coating than Comparative Example 2. However, a comparison of the SEM image of Fig. 2with the SEM image of Fig. 3 showing the coating obtained with Example 4 according to the present invention shows that the process according to Example 4 produces a coating which is even more smooth than the coating made according to Comparative Example 1.

[0099] The process according to this invention is useful for making a surface modified coating such as an adhesion promoter or an antifog coating; an optical coating such as a reflective or antireflective coating, a light spectrum management coating, or UV protection coating; a chemical resistant coating; an abrasion-resistant coating; or a gas barrier coating. Examples of potential end use applications include online coating of extruded plastic film, sheet, laminates and molded articles useful in architectural glazing, glazing panels, solar collectors, appliances, optical consumer products and devices, packaging, signage, and transportation.

CLAIMS

1. A process for coating or modifying a substrate comprising:

    (a) providing a substrate having at least one surface;

    (b) providing a gaseous mixture adjacent the at least one surface of the substrate of (a);

    (c) generating a plasma in the gaseous mixture of (b), and

    (d) allowing the plasma of (c) to form a solid deposit on the at least one surface of the substrate,

    wherein the gaseous mixture comprises:

    at least 35 volume-percent nitrogen gas;

    at least 50 ppm of at least one gaseous precursor;

    optionally an oxidizing gas for the gaseous precursor; and

    up to a 1.5:1 volume ratio of at least one rare gas relative to nitrogen gas, the rare gas comprising at least 1 volume-percent helium gas, at least 1 volume-percent neon gas, or at least 3 volume-percent argon gas, or a mixture thereof,

    each volume-percent based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

2. The process according to claim 1, wherein the volume ratio of rare gas to nitrogen gas in the gaseous mixture of (b) is 1:1 or less at 20°C and 101 kPa pressure.

3. The process according to claim 1, wherein the volume ratio of rare gas to nitrogen gas in the gaseous mixture of (b) is 1:2 or less at 20°C and 101 kPa pressure.

4. The process according to any one of the preceding claims, wherein the gaseous mixture of (b) comprises helium in an amount in the range from 1 to 37 volume-percent based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

5. The process according to any one of the preceding claims, wherein the gaseous mixture of (b) comprises helium in an amount in the range from 2 to 10 volume-percent based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

6. The process according to any one of claims 3 to 5, wherein the gaseous mixture of (b) contains at least 45 volume-percent nitrogen gas based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

7. The process according to any one of the preceding claims, wherein the gaseous mixture of (b) contains the optional oxidizing gas in an amount of at least 5 volume-percent based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

8. The process according to claim 7, wherein the oxidizing gas comprises oxygen, nitrous oxide, ozone, nitric oxide, or nitrogen tetraoxide, or a combination thereof.

9. The process according to claim 7 or 8, wherein the gaseous mixture of (b) comprises at least 10 volume-percent oxygen gas based on the total volume of the gaseous mixture at 20°C and 101 kPa pressure.

10. The process according to any one of the preceding claims, wherein the gaseous precursor comprises at least one silicon-containing compound represented by the chemical formula (I):

$$R_3Si[X\text{-}Si(R')_2]_rR'' \qquad (I)$$

wherein R, R', and R'', independently at each occurrence, represent -H, -OH, a C_{1-10} hydrocarbyl group, or a C_{1-10} hydrocarbyloxy group, X represents –O- or –N(R'''')-, wherein R'''', independently at each occurrence, represents –H or a C_{1-10} hydrocarbyl group, and r represents zero or a number in the range from 1 to 10.

11. The process according to claim 10, wherein the gaseous precursor comprises a silane or siloxane compound.

12. The process according to any one of claims 1 to 9, wherein the gaseous precursor comprises at least one metal-containing compound represented by the chemical formula (II):

$$MR_aX_b \qquad (II)$$

wherein M is a metal represented by Zn, Sn, Al, and Ti; R, independently at each occurrence, represents -H, -OH, a C_{1-10} hydrocarbyl group, or a C_{1-10} hydrocarbyloxy group, X represents a halogen including Cl or Br; and "a" and "b" each represent whole numbers of R and X moieties, previously described, in the range from zero to the valence of M, provided that the total of a + b equals the valence of the metal M; or a volatile salt thereof.

13. The process according to claim 12, wherein the at least one metal-containing compound comprises diethyl zinc, dimethyl zinc, zinc acetate, titanium tetrachloride, dimethyltin diacetate, zinc acetylacetonate, zirconium hexafluoroacetylacetonate, zinc carbamate, trimethyl indium, triethyl indium, cerium (IV) (2,2,6,6-tetramethyl-3,5-heptanedionate), and mixtures thereof

14. The process according to any one of the preceding claims, wherein the pressure of the gaseous mixture is 101.3 kPa +/- 20 kPa.

15. The process according to any one of the preceding claims, wherein the plasma is generated by a dielectric barrier discharge apparatus operating at a) at a frequency of at least 2 kHz and not greater than 100 kHz and b) at a power density in the range from 1 W/cm^2 to 140 W/cm^2.

16. The process according to claim 15, wherein the power density is in the range from 9 W/cm^2 to 40 W/cm^2.

17. The process according to claim 16, wherein the solid deposition is deposited on the substrate at a rate of at least 0.008 mg / ($cm.^2$ * minute).

18. The process according to claim 16, wherein the solid deposition is deposited on the substrate at a rate of at least 0.06 mg / ($cm.^2$ * minute).

19. The process according to any one of the preceding claims, wherein the substrate comprises at least one polymer selected from the group consisting of polycarbonates, polyurethanes, poly(meth)acrylates, polypropylenes, polyethylenes, ethylene/α-olefin copolymers, styrene-acrylonitrile copolymers, polyethylene terephthalates, and polybutylene terephthalates.

20. A coated substrate obtainable by the process according to any one of the preceding claims.

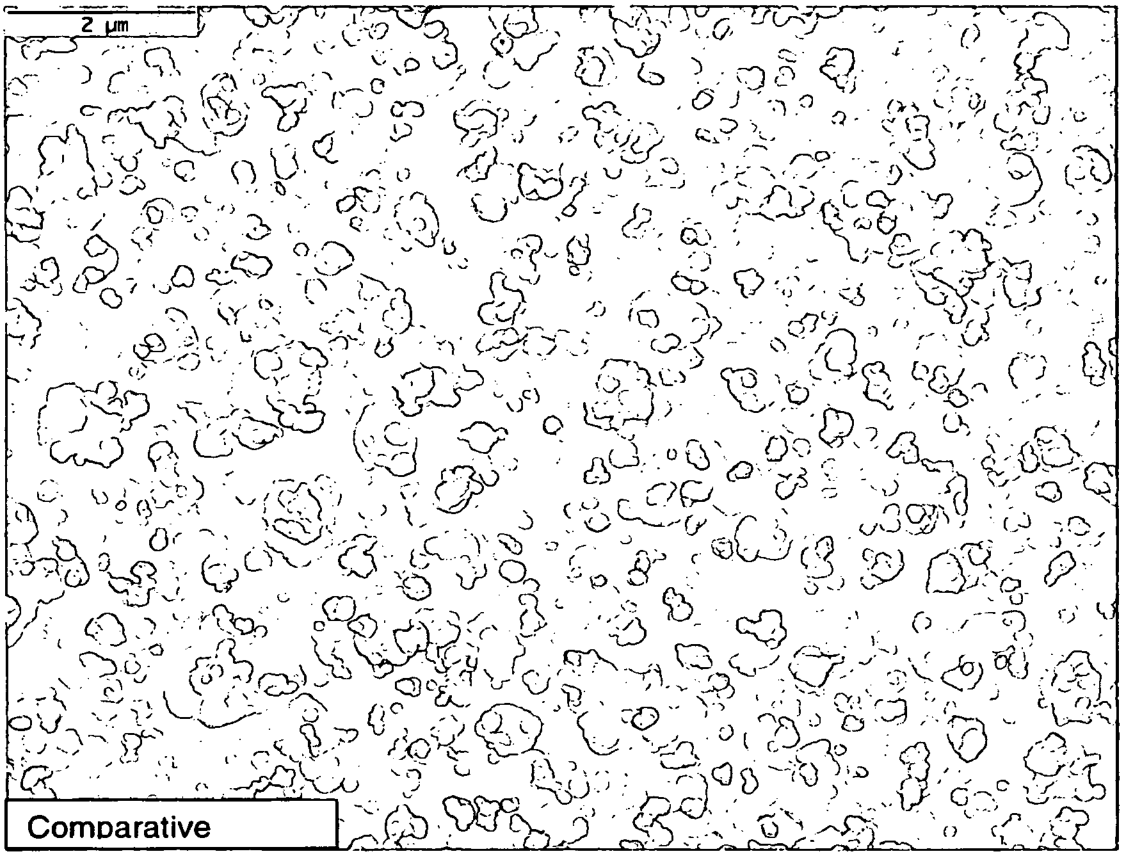


Fig. 1

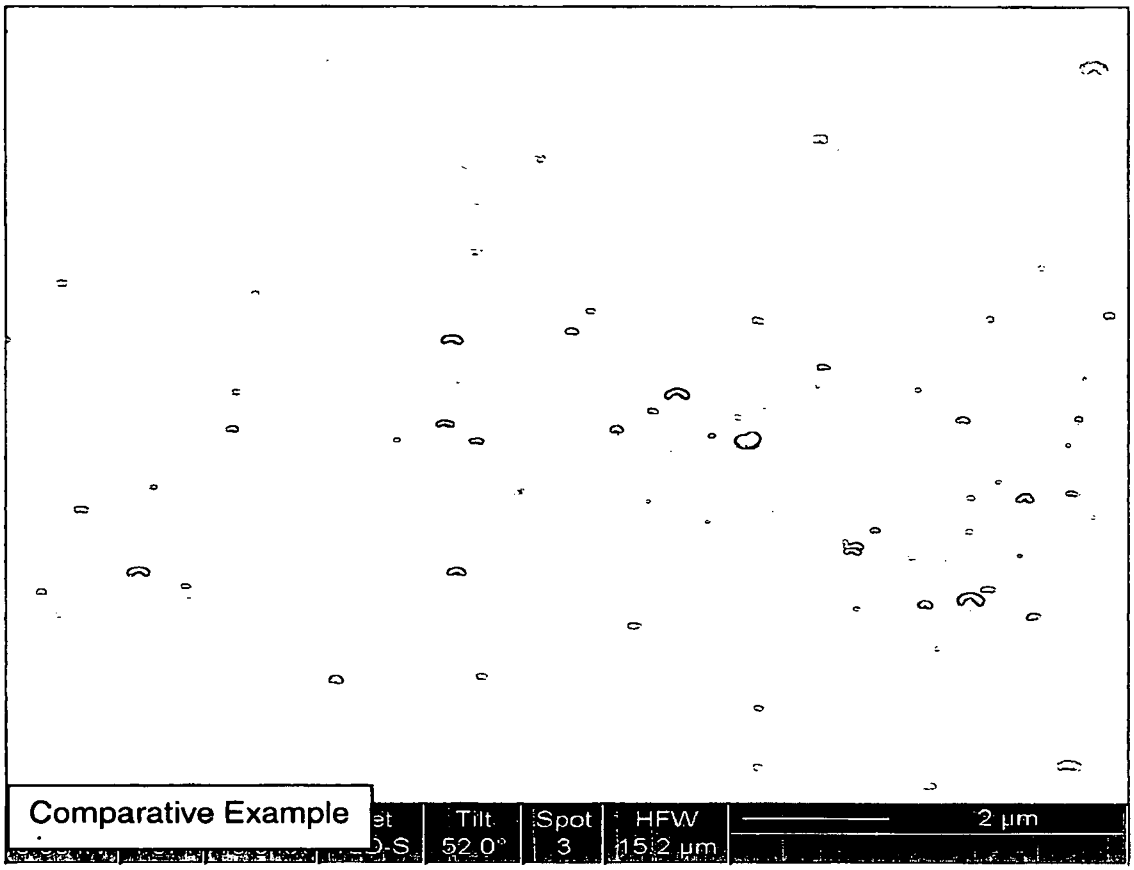


Fig. 2

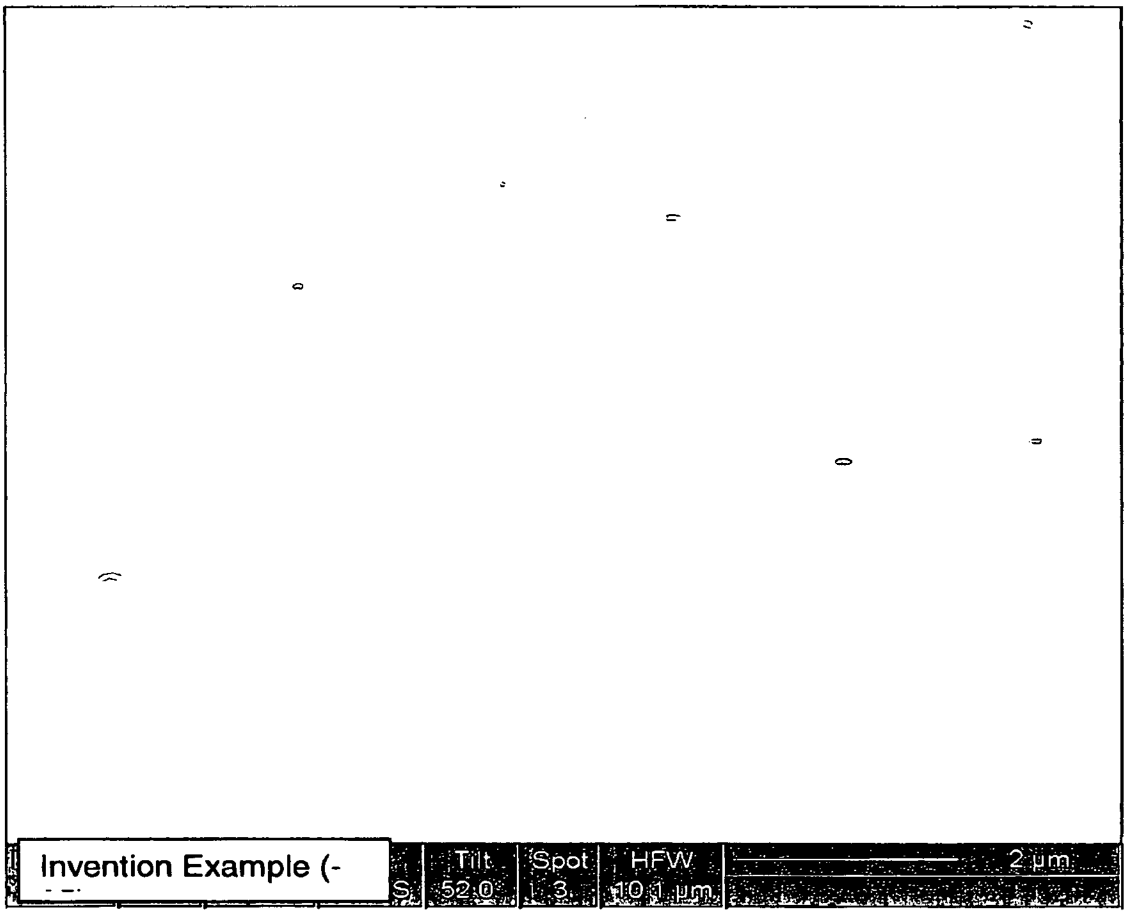


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/021038

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/503 C23C16/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

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

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

EPO-Internal, COMPENDEX, INSPEC, 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	SCHMIDT-SZALOWSKI K ET AL: "Thin films deposition from hexamethyldisiloxane and hexamethyldisilazane under dielectric-barrier discharge (DBD) conditions" PLASMAS AND POLYMERS PLENUM USA, vol. 5, no. 3-4, December 2000 (2000-12), pages 173-190, XP002465444 ISSN: 1084-0184 table 1 -----	1-11, 14-20

-/--

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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
22 January 2008	04/02/2008

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, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hoyer, Wolfgang

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/021038

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ULEJCZYK B ET AL: "Deposition of silicon oxide film from tetraethoxysilane using a pulsed dielectric barrier discharge" CZECHOSLOVAK JOURNAL OF PHYSICS, KLUWER ACADEMIC PUBLISHERS-CONSULTANTS BUREAU, NE, vol. 56, no. 2, 1 October 2006 (2006-10-01), pages B1383-B1390, XP019448140 ISSN: 1572-9486 the whole document -----	1-20
X	WO 2006/087941 A (KONICA MINOLTA HOLDINGS INC [JP]; FUKUDA KAZUHIRO [JP]; ARITA HIROAKI) 24 August 2006 (2006-08-24) paragraphs [0032] - [0057], [0071] - [0074], [0129] - [0141] & EP 1 849 593 A (KONICA MINOLTA HOLDINGS INC [JP]) 31 October 2007 (2007-10-31) -----	1-20
E	WO 2007/133378 A (DOW GLOBAL TECHNOLOGIES INC [US]; GABELNICK AARON M [US]; HAEMHOUTS PA) 22 November 2007 (2007-11-22) the whole document -----	1-20
A	MASSINES ET AL: "Atmospheric pressure plasma deposition of thin films by Townsend dielectric barrier discharge" SURFACE AND COATINGS TECHNOLOGY, ELSEVIER, AMSTERDAM, NL, vol. 200, no. 5-6, 21 November 2005 (2005-11-21), pages 1855-1861, XP005173234 ISSN: 0257-8972 the whole document -----	1-20
A	WO 2004/030019 A (FUJI PHOTO FILM BV [NL]; DE VRIES HINDRIK WILLEM [NL]; MORI FUYUHIKO [) 8 April 2004 (2004-04-08) page 10, line 23 - page 13, line 28; example 3 -----	1-20
A	PEETERS P ET AL: "Uniform glow-like atmospheric DBD for surface treatment and deposition" PROC ANNU TECH CONF SOC VAC COATERS; PROCEEDINGS, ANNUAL TECHNICAL CONFERENCE - SOCIETY OF VACUUM COATERS; SVC, SOCIETY OF VACUUM COATERS 48TH ANNUAL TECHNICAL CONFERENCE PROCEEDINGS 2005, 2005, pages 224-228, XP009094763 the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2007/021038

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 2006087941	A	24-08-2006	EP 1849593	A1	31-10-2007
EP 1849593	A	31-10-2007	WO 2006087941	A1	24-08-2006
WO 2007133378	A	22-11-2007	NONE		
WO 2004030019	A	08-04-2004	AU 2003276023	A1	19-04-2004
			EP 1403902	A1	31-03-2004
			JP 2006503406	T	26-01-2006
			US 2006147648	A1	06-07-2006