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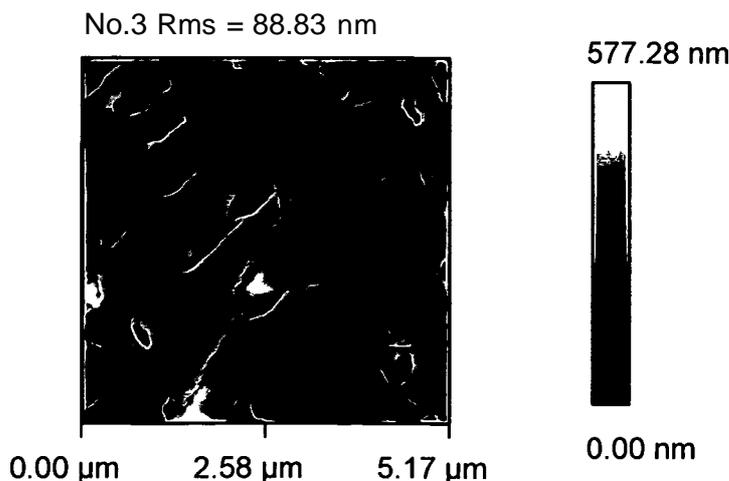
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(54) **Title:** ARTICLES WITH SUPER-HYDROPHOBIC AND-OR SUPER HYDROPHILIC SURFACES AND METHOD OF FORMATION

No.3 Rms = 88.83 nm

Fig. 3

0.00 μm   2.58 μm   5.17 μm

577.28 nm

0.00 nm

(57) **Abstract:** The present invention is related to a chemical vapor deposition method of depositing layers of materials to provide super-hydrophilic surface properties, or super- hydrophobic surface properties, or combinations of such properties at various locations on a given surface. The invention also relates to electronic applications which make use of super-hydrophobic surface properties, and to biological applications which make use of super-hydrophilic surface properties.

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[0001]   **ARTICLES WITH SUPER-HYDROPHOBIC AND-OR SUPER-HYDROPHILIC SURFACES AND METHOD OF FORMATION**

3   [0002]   The present application claims priority under two provisional applications,

4   Application Serial No. 60/921,61 8, filed April 2, 2007, and titled: "CVD Method Of

5   Surface Treatment To Provide Super-Hydrophobic and Super-Hydrophilic Properties",

6   and Application Serial No. 60/926,205, filed April 24, 2007, and titled: "Method Of

7   Forming Super-Hydrophobic And Super-Hydrophilic Films And Articles Having The

8   Films". Each of these provisional applications is incorporated by reference herein in its

9   entirety. In addition, the present application is related to a series of patent applications

10   pertaining to the application of thin film coatings on various substrates, particularly

11   including the following applications, each of which is hereby incorporated by reference in

12   its entirety: U.S. Application Serial No. 10/759,857, filed January 17, 2004, and titled:

13   Apparatus And Method For Controlled Application Of Reactive Vapors To Produce Thin

14   Films and Coatings; U.S. Application Serial No. 11/1 12,664, filed April 21, 2005, and

15   titled: Controlled Deposition Of Multilayered Coatings Adhered By An Oxide Layer;

16   U.S. Application No. 11/295,129, filed December 5, 2005, and titled: Controlled Vapor

17   Deposition Of Biocompatible Coatings Over Surface Treated Substrates; U.S.

18   Application Serial No. 10/912,656, filed August 4, 2004, and titled: Vapor Deposited

19   Functional Organic Coatings; U.S. Application Serial No. 11/123,487, filed May 5, 2005,

20   and titled: Controlled Vapor Deposition Of Biocompatible Coatings For Medical

21   Devices; U.S. Patent Application Serial No. 11/447,186, filed June 5, 2006, and titled:

22   Protective Thin Films For Use During Fabrication Of Semiconductors, MEMS, and

23   Microstructures; and U.S. Patent Application Serial No. 60/930,290, filed May 14 2007,

24   and titled: "Durable Multi-Layer Coatings And Coated Articles".

1   [0003]   **BACKGROUND O F THE INVENTION**

2   [0004]   1. Field of the Invention

3   [0005]   The present invention is related to a method of creating super hydrophilic

4   surfaces, super hydrophobic surfaces, and combinations thereof. In addition, the

5   invention is related to creation of such surfaces on consumer products such as, for

6   example, electronic devices, optical devices, and others, to enhance performance of the

7   product.

8   [0006]   2. Brief Description of the Background Art

9   [0007]   This section describes background subject matter related to the invention, with

10   the purpose of aiding one skilled in the art to better understand the disclosure of the

11   invention. There is no intention, either express or implied, that the background art

12   discussed in this section legally constitutes prior art.

13   [0008]   Super-hydrophobic and super-hydrophilic materials are typically characterized

14   by reference to a water contact angle with the surface of the material. A water contact

15   angle which is greater than about 120 degrees is typically considered to be indicative of a

16   super hydrophobic material. Some of the more advanced super hydrophobic materials

17   exhibit a water contact angle in the range of about 150 degrees. A super-hydrophilic

18   material is typically characterized by a water contact angle of 0 (zero) degrees, which

19   results in an instantaneous wetting of the surface of such a material.

20   [0009]   Super hydrophobic surface properties are very desirable in a number of

21   consumer product applications, as the surface is protected from wetting and

22   contamination. For example, an electronic device which might otherwise be shorted out

23   upon becoming wet may be treated to provide a protective hydrophobic surface which

24   keeps the device clean and dry.

25   [0010]   Super hydrophobic surfaces may be created by processing of an existing

26   surface. Typical methods of converting material surfaces to become super hydrophobic

27   include, for example: 1) Etching the existing surface to create specific nano-patterns

(patterns which are in the nanometer size range), and subsequently coating the surface

with a hydrophobic coating. 2) Roughening the substrate surface using techniques

known in the art, and functionalizing the resulting surface by applying a hydrophobic

coating. 3) Growing a rough (or porous) film from solutions containing nano-particles or

polymers in a way which creates a rough and hydrophobic surface on the material.

[0011]   Generally hydrophobic surfaces have been created in recent years by

deposition of common fluorocarbon coatings over a surface. Such fluorocarbon coatings

may be created by application of self-assembled perfluorocarbon monolayers (fluorine-

containing SAMs), for example. However such surfaces tend to have a water contact

angle which is less than about 120 degrees. To obtain a higher water contact angle, it

appears to be necessary to texturize the surface prior to application of such a fluorocarbon

coating. Although a substrate modified to contain a nano-pattern alone can provide a

super-hydrophobic behavior (if the material is hydrophobic to begin with) with respect to

a given liquid, a combination of both the nano-patterned surface with a hydrophobic

surface finish is helpful in providing and maintaining long term super-hydrophobic

behavior of a surface.

[0012]   Most known man made materials are either hydrophilic or hydrophobic, with

their respective surface wetting properties varying within a wide range. Roughening and

texturing of a material surface for the purpose of creating a super-hydrophobic or a super-

hydrophilic surface is typically done using one of the following methods, each of which

has respective advantages and disadvantages.

[0013]   1. Micro-nano-patterning by material removal: a) The surface may be

chemically etched. For example, XeF_2 may be used to pattern etch silicon, or HF may be

used to pattern etch a silicon oxide. b) The surface may be patterned by plasma etching,

such as that used in photo and nano-imprint lithography. c) The surface may be random

patterned (roughened) using ion beams, biased plasmas, or laser ablation. d) The surface

may be patterned by directly writing a pattern using an electron beam or a laser, or may be

1   patterned through a mask using plasma etching.

2   [0014]   2. Surface Texturing: a) The surface may be thermally embossed or

3   imprinted when the material is a thermoplastic. b) The surface may be laser treated when

4   the material is polymeric, c) Inorganic material surfaces may be high temperature

5   annealed, such as in the high temperature annealing of polysilicon.

6   [0015]   3. Material deposition or treatment: a) A liquid coating of colloidal nano-

7   particles or a gel may be spin-coated over the surface of a substrate material, b) A porous

8   surface layer may be created over a material by casting of a polymeric precursor in

9   combination with a non-miscible substance, such as with moisture, for example, c) A

10   metal surface may be treated using micro-arc oxidation.

11   [0016]   The effectiveness of coating of a textured or roughened surface to produce a

12   super-hydrophobic behavior is typically limited by adhesion of the super-hydrophobic

13   coating material to the substrate material surface. Therefore, many materials (e.g.

14   plastics, polymers, and certain noble metals) may require the use of adhesion layers such

15   as silica, alumina, or other adhesion promoters which are applied over the substrate

16   material surface prior to application of a super-hydrophobic coating material over a

17   textured or roughened surface. Physical vapor deposition (PVD), chemical vapor

18   deposition (CVD), atomic layer deposition (ALD) and other deposition techniques may be

19   used to apply an adhesion-promoting layer. The surface of an adhesion-promoting layer

20   applied in such a manner is typically smooth and replicates the underlying material

21   surface topography.

22   [0017]   Bharat Bhushan et al., in U.S. Application No. 11/094,867, filed March 31,

23   2005, and titled "Hydrophobic Surface With Geometric Roughness", describes the

24   texturing of a surface to form asperities structures, with subsequent coating or

25   functionalizing of the geometrically patterned surface to produce hydrophobic properties.

26   The Abstract teaches: "A hydrophobic surface comprising a substrate and a roughened

27   surface structure oriented on the substrate material is provided. The substrate comprises a

1   surface, which is at least partially hydrophobic with a contact angle to liquid of 90 degrees

2   or greater. The roughened surface structure comprises a plurality of asperities arranged in

3   a geometric pattern according to a roughness factor, wherein the roughness factor is

4   characterized by a packing parameter p that equals the fraction of the surface area of the

5   substrate covered by the asperities. The p parameter has a value from between about 0.5

6   and 1." An exemplary drawing of such a surface shows hemispherically topped pyramidal

7   asperities.

8   [0018]   N. Zhau et al., in an article entitled "Fabrication of Biomimetic

9   Superhydrophobic Coating with a Micro-nano-binary Structure", Macromolecular Rapid

10   Communication, 205, 26, 1075-1080, describe fabrication of a super-hydrophobic coating

11   by casting a polymer solution of bisphenol A polycarbonate (PC) in the presence of

12   moisture. The method comprises a controlled solvent evaporation from the casting

13   solution in the presence of moisture. A porous polymer surface is formed with a micro-

14   nano-binary structure which is said to be similar to that of a lotus leaf.

15   [0019]   The authors teach that they clearly showed from the experimental results that

16   humid air was a crucial element for the formation of the hierarchiacal structure. In

17   addition, the authors propose that casting a polymer solution in the presence of moisture

18   has frequently been used in the fabrication of porous polymer membranes. The influence

19   of moisture on the morphology of the resulting membrane is said to largely depend on the

20   miscibility of the solvent with water. With a water-immiscible solvent, water micro-

21   droplets will condense on the solution surface due to evaporation cooling and then act as a

22   template. After solidification, a honeycomb-patterned porous film is said to be formed.

23   The paper provides illustrations of SEM images of coatings cast at room temperature at

24   different relative humidity, ranging from 20 % up to 75 %.

25   [0020]   In an article by L. Zhai, et al., titled "Stable Superhydrophobic Coating from

26   Polyelectrolyte Multilayers", Nanoletter, 2004, V4, 1349 - 1353, the authors describe the

27   formation of super-hydrophobic surfaces by coating a honeycomb-like surface covered

1   with silica nano-particles. The coating applied over the surface is formed by a chemical

2   vapor deposition (CVD) of tridecafiuoro- 1,1,2,2-tetrahydrooctyl)- 1-trichlorosilane (a

3   semifluorinated silane). Superhydrophobicity is said to have been achieved by coating

4   this highly textured multilayer surface with a semifluorinated silane. The super

5   hydrophobic surface is said to maintain its super hydrophobic character even after

6   extended immersion in water.

7   [0021]   In one embodiment, the authors describe a layer-by layer process of forming

8   multilayers which fabricate conformal thin films. The layer-by-layer film application is

9   said to be useful for any surface amenable to a water-based adsorption process used to

10   construct the polyelectrolyte multilayers. In particular, the authors claim to have

11   discovered that, by using an appropriate combination of acidic treatments PAH/PAA

12   8.5/3.5, films can be induced to form pores on the order of 10 microns and a honeycomb-

13   like structure on a surface. PAH is poly(allylamine hudrochloride), and PAA is poly

14   (acrylic acid). The surface roughness of such films may be 400 nm, for example. A

15   dense film is created, followed by staged low pH treatments, followed by crosslinking at

16   180 ^{0}C for 2 hours. Subsequently, an SiO_2 nanoparticle deposition is carried out, in

17   which 50 nm SiO_2 nanoparticles are deposited by alternating dipping of the substrates into

18   an aqueous suspension of negatively charged nanoparticles and an aqueous PAH solution,

19   followed by a final dipping of the substrate into the nanoparticle suspension. The surface

20   is then modified by the CVD coating deposition described above. Finally, the coated

21   substrate is treated using a 2 hour baking at 180 ^{0}C to remove unreacted semifluorinated

22   silane.

23   [0022]   With respect to the production of super hydrophobic surfaces on useful

24   articles, there are nearly unlimited potential applications. One area of particularly

25   beneficial use is to reduce the contamination and corrosion of electronic boards of the

26   kind used in common electronic products. Many failures of electronic consumer products

27   are due to corrosion and electric shorts caused by accidental wetting or atmospheric

1   moisture condensation on components and wiring leads of electronic boards. In addition,

2   spill accidents are statistically responsible for about 20 % of all portable electronics

3   replacements. Marine electronics products and products exposed to wet or humid

4   conditions are particularly vulnerable to such failures. Electronic board reliability in

5   humid and wet environment is also critical to performance of consumer electronics

6   portable devices such as GPS, cell phones, PDA assistants, computers, digital cameras,

7   video games and others.

8   [0023]   Due to improvements in materials and electronic device packaging

9   technologies, individual device (chip) reliability has reached new levels, above 99.95 %.

10   However, the performance of electronic boards, board interconnects and mounting remain

11   as critical bottlenecks for product reliability. Surfaces of most electronic board materials

12   and components are hydrophilic, which promotes moisture condensation and wetting.

13   Therefore, device performance and reliability can be compromised when electronic

14   boards are exposed to liquids or excessive moisture during everyday use. Environmental

15   contaminants which form ionic solutions in a wet environment can result in leakage or

16   shorts between the device leads. Corrosion over time can further damage electrical

17   connections and render devices non-operational. Encapsulation of the entire electronic

18   board with a moisture protective coating can prevent such damage. However, due to a

19   relatively high cost of such protective coatings, and other disadvantages such as, for

20   example, poor heat dissipation, only specialty and military use electronics use board level

21   protection in the form of a moisture-resistant coating. Parylene, silicone, epoxy,

22   urethane, and other similar coatings have been used in the past, each of them having a

23   number of disadvantages and limitations.

24   [0024]   Metal oxides, and in particular aluminum oxide (alumina) and titanium oxide

25   (titania) coatings are known to provide moisture protection and are of particular interest

26   as replacements for the kinds of coatings such as the urethane, epoxy, silicone and

27   parylene coatings mentioned above. The metal oxide coatings can be deposited by means

1   such as physical vapor deposition (PVD) or atomic layer deposition (ALD) methods.

2   However, the coatings generated are not super hydrophobic in nature.

3   **[0025]**   Featherby et al., in U.S. Patent No. 6,963,125, issued November 8, 2005 and

4   entitled "Electronic Device Packaging", describe an encapsulation method for electronic

5   packaging. The encapsulation is provided by a coating consisting of two layers: 1) an

6   inorganic layer preventing moisture intake, and 2) an outside organic layer protecting the

7   inorganic layer. Both layers are said to be integrated with an electronic device plastic

8   package. Several inorganic materials, such a silicon nitride, aluminum nitride, titanium

9   nitride and other oxides are suggested for formation of the inorganic layer. These layers

10   may be deposited by PVD, CVD, or ALD, to provide a first continuous layer over a

11   substrate. Subsequently, an organic layer, said to be preferably Parylene C (Col. 10) is

12   applied directly over the inorganic layer. The organic layer has the primary function of

13   protecting the brittle inorganic coating during manufacturing steps such as injection

14   molding.

15   **[0026]**   The use of a dual layer of an inorganic alumina film in combination with an

16   overlying alkylaminosilane hydrophobic coating attached to alumina hydroxyl groups was

17   proposed for wear and stiction protection in micro-electro-mechanical (MEMS) devices in

18   U.S. Patent Application No. 10/910525 filed by George et al. on August 2, 2004. The

19   application, is entitled "Al_2O_3 Atomic Layer Deposition to Enhance the Deposition of

20   Hydrophobic or Hydrophilic Coatings on Micro-electromechanical Devices". In addition,

21   George et al. proposed the use of ALD alumina films as moisture and gas barriers on

22   polymer substrate surfaces in U.S. Application No. 10/482,627, filed on July 16, 2002,

23   and entitled "Method of Depositing an Inorganic Film on an Organic Polymer".

24   **[0027]**   With the development of electroluminescent devices, flat panel displays,

25   organic light emitting diodes (OLEDS), and flexible electronics, there is even a stronger

26   need to protect such devices from performance degradation due to oxidation and moisture

27   corrosion. PVD and ALD alumina films have been tried extensively for such application.

1   However, the single or dual layer protective coatings were found to be inadequate in many

2   cases. Subsequently, various multilayer film laminates have been explored and are

3   currently being considered as a hermetic glass package replacement for use in devices

4   requiring a high degree of protection, for example OLEDs. Haskal et al., in U.S. Patent

5   No. 5,952,778, issued September 14, 1999, and entitled "Encapsulated Organic Light

6   Emitting Device", proposed an encapsulation scheme to prevent the oxidation and

7   degradation of OLED devices due to exposure to oxygen, water, and other contaminants.

8   The protective covering comprises three contiguous layers, which include 1) a first layer

9   of thin passivation metal; 2) a second layer of thin film deposited dielectric material such

10   as silicon dioxide or silicon nitride; and, 3) a third layer of a hydrophobic polymer.

11   [0028]   Park et al., in U.S. Patent No. 6,926,572, issued August 9, 2005, entitled "Flat

12   Panel Display Device and Method of Forming Passivation Film in the Flat Panel Display

13   Device" teach a low temperature protective barrier film which is a combination of

14   multiple organic and inorganic films. Simultaneous vapor deposition of silicon

15   tetrachloride and dimethyldichlorosilane onto a glass substrate is said to result in a

16   hydrophobic coating comprised of cross-linked polydimethylsiloxane which may then be

17   capped with a fluoroalkylsilane (to provide hydrophobicity). The substrate is said to be

18   glass or a silicon oxide anchor layer deposited on a surface prior to deposition of the

19   cross-linked polydimethylsiloxane. The substrates are cleaned thoroughly and rinsed

20   prior to being placed in the reaction chamber.

21   [0029]   Some methods useful in applying layers and coatings to substrates have been

22   briefly described above. There are numerous other patents and publications which relate

23   to the deposition of functional coatings on substrates, but which appear to be more

24   distantly related to the present invention. To provide a monolayer or a few layers of a

25   continuous functional coating on a substrate surface so that the surface will exhibit

26   particular functional properties it is necessary to tailor the coating precisely. Without

27   precise control of the deposition process, the coating may lack thickness uniformity and

1   surface coverage. The presence of non-uniformities may result in functional

2   discontinuities and defects on the coated substrate surface which are unacceptable for the

3   intended application of the coated substrate.

4   [0030]   U.S. Patent Application Serial No. 10/759,857 of the present applicants

5   describes one kind of processing apparatus which can provide specifically controlled,

6   accurate delivery of precise quantities of reactants to a processing chamber, as a means of

7   improving control over a CVD coating deposition process. The subject matter of the '857

8   application is hereby incorporated by reference in its entirety.

9   [0031]   SUMMARY

10 [0032]   The present invention is related to a chemical vapor deposition method of

11 coating and treating materials to provide super-hydrophilic surface properties, or super-

12 hydrophobic surface properties, or combinations of such properties at various locations on

13 a given surface.

14 [0033]   The invention also relates to electronic applications which make use of the

15 super-hydrophobic surface properties to protect objects, such as electronic boards and

16 components of electronic devices. In particular, the boards and components are protected

17 from damage due to accidental and environmental factors, especially due to wetting,

18 spills, and water condensation.

19 [0034]   One skilled in the art of biological applications or optical applications can

20 envision a large number of instances which may make use of super-hydrophilic surface

21 properties, or which may make use of a surface which comprises both areas which are

22 super-hydrophilic and areas which are super-hydrophobic.

23 [0035]   One aspect of the present invention pertains to a chemical vapor deposition

24 method of treating and coating materials to provide the desired super-hydrophobic or

25 super-hydrophilic properties. A surface topography is created using a CVD deposition of

26 particles nucleated in situ by reacting two or more vaporous precursors in the gas phase to

1   form nano-particles. The nano-particles are subsequently deposited onto the substrate,

2   forming a rough surface topography. The gas phase reaction processing parameters are

3   controlled so that the size of the resulting surface topography is carefully controlled. As a

4   method of monitoring the effect of various processing parameters on the resulting surface

5   topography, a surface roughness in nanometers RMS (Random Mean Square) is measured

6   by AFM (Atomic Force Microscopy). By varying the process parameters, it was possible

7   to control the RMS from a few up to hundreds of nanometers. The processing parameters

8   which were controlled included the amount of reactants charged to the processing

9   chamber, the relative ratios of reactants, the reaction pressure, time, and temperature, and

10   the number of reaction cycles, by way of example and not by way of limitation.

11   [0036]   In a typical embodiment rough metal oxide films were produced by nucleating

12   metal oxide nano-particles in a gas phase and depositing them onto the substrate, hi the

13   past, such spontaneous gas phase reactions have been purposely avoided because they

14   were considered to produce undesirable particles due to gas phase nucleation. In the

15   present instance, a method of controlling process variables has been developed and the

16   gas reaction which was previously considered to be a problem has been purposely used to

17   form nano-particles. The reaction parameters are selected to control the rate of nano-

18   particle formation and consequently to obtain the desired size of the features, which is

19   illustrated by the surface roughness measurement. Examples of the reaction parameters

20   and their impact on surface roughness are described in the detailed description. RMS

21   values ranging from about 8.5 nm to 124 run have been obtained. Figure 1 shows the 8.53

22   nm RMS surface topography of a single crystal silicon substrate covered with nano-

23   particles deposited from a reactive vapor phase. Figure 2 shows the 13.3 nm RMS

24   surface topography of the same substrate covered with nano-particles deposited from a

25   reactive vapor phase. Figure 3 shows the 88.83 nm RMS surface topography of the same

26   single crystal silicon substrate covered with nano-particles deposited from a reactive

27   vapor phase. Figure 4 shows the 124 nm RMS surface topography of the same substrate

1   covered with nano-particles deposited from a reactive vapor phase. The differences in

2   surface topography shown in Figures 1 - 4 were obtained by variation of the processing

3   parameters described above.

4   [0037]   Organometallics, metal chlorides, highly reactive chlorosilanes and other

5   vaporous precursors can be used in vapor phase reactions to produce similarly rough

6   surface topography. Control of the partial pressures of the reactants in the processing

7   chamber, the reaction pressure, temperature and time, and the number of

8   nucleation/deposition cycles enables the formation of sized nano-particles and surface

9   roughness features. hi the case of insufficient gas phase reaction, the resulting surface

10   roughness is too small (RMS is less than about 5 run), and the contact angle is degraded

11   to an angle far below the 150 degrees which is considered to be a super-hydrophobic

12   surface. In the case where there is too much gas phase reaction, the resulting surface

13   roughness becomes too large (RMS is greater than about 100 nm), with the layer of

14   deposited material being very fluffy and not well adhered to the substrate. The average

15   thickness of the layer of deposited nano-particles typically ranges from about 100 Å to

16   about1,000 Å. This thickness of the layer may be controlled by the number of sequential

17   nano-particle deposition cycles. A layer deposited using organometallic, metal chloride,

18   and/or a highly reactive chlorosilane precursor forms a super-hydrophilic surface layer.

19   [0038]   To produce a super-hydrophobic surface which is maintained over time after

20   exposure to environmental conditions, the surface of the deposited nanoparticles is

21   typically coated (functionalized) with a self assembling monolayer of a fluorine-

22   containing polymer.

23   [0039]   An alternative to the use of a fluorocarbon coating over the surface of the

24   deposited nano-particle layer is to include, in-situ in the gas phase mixture, an alkylsilane,

25   alkylaminosilane, perfluoroalkylsilane or similar precursor, as a part of the reactive

26   precursor materials used to form the nano-particles. For example, an organometallic,

27   metal chloride, or highly reactive chlorosilane reactive precursor may be used as a

1   reaction precursor in combination with an alkylsilane, alkylaminosilane, or

2   perfluoroalkylsilane.

3   [0040]   When the surface of a substrate to which the super-hydrophobic coating is

4   applied is one which is difficult to adhere to, such as various polymeric materials and

5   noble metals, by way of example and not by way of limitation, conventional spin-on,

6   PVD, CVD, or ALD metal oxides and silicon oxides, as well as the corresponding nitrides

7   may be deposited as adhesion layers prior to deposition of the super-hydrophobic surface

8   layer.

9   [0041]   A super-hydrophobic surface can subsequently be applied over the surface of

10   the adhesion layer. The super-hydrophobic surface can be tailored to a desired degree of

11   hydrophobicity or can be patterned to exhibit super-hydrophobic properties in some areas

12   and superhydrophilic properties in other areas by selectively removing the hydrophobic

13   coating from an underlying hydrophilic substrate surface. Masking or patterning using

14   lithographic techniques can be used in combination with oxygen etching or UV radiation

15   exposure to selectively remove the hydrophobic coating from particular areas on a

16   substrate surface.

17   [0042]   In another embodiment, a coating of a hydrophilic functional polymeric layer

18   such as bis-trichlorosilyl-ethane or methoxy(polyethylene glycol)MPEG, for example,

19   may be deposited over a nano-particle deposited super-hydrophilic surface layer to

20   stabilize the surface and maintain the super-hydrophilic surface property.

21   [0043]   There are many applications for super-hydrophobic surface layers. One

22   embodiment is in the area of protective films over the surfaces of electronic devices, such

23   as digital cameras, cell phones, digital music and video players, portable computers,

24   marine electronics and other devices which require continuous operation in adverse

25   environmental conditions, and resistance to occasional exposure to water or other liquids.

26   A typical protective film includes a first layer of a moisture barrier material, which may

27   be a single or multi-layer of a metal oxide or nitride, for example, and not by way of

1   limitation. A super-hydrophobic film of the kind described above is deposited over the

2   surface of the moisture barrier material. A s previously discussed, the metal oxide or

3   nitride may be formed from reactive precursor materials which are also used in

4   combination with other precursor materials to form the super-hydrophobic layer.

5   [0044]   There are many applications for super-hydrophilic surface layers. Some of the

6   most valuable applications are for use in biological applications, microfluidic devices and

7   optical application (anti-fog coatings for lenses and mirrors, for example).

8   [0045]   BRIEF DESCRIPTION   OF THE DRAWINGS

9   [0046]   Figure 1 shows an AFM image of an 8.53 ran RMS surface topography

10 obtained on a single crystal silicon substrate, by deposition of a layer of nano-particles

11 from a reactive vapor phase comprising trimethyl aluminum (TMA) and water vapor.

12 [0047]   Figure 2 shows an AFM image of a 13.3 run RMS surface topography

13 obtained on the same single crystal silicon substrate by deposition of a layer of nano-

14 particles from a reactive vapor phase comprising TMA and water vapor, where the

15 amount of TMA was increased by about 17 % over the amount which was present during

16 the formation of the nano-particles layer shown in Figure 1.

17 [0048]   Figure 3 shows an AFM image of an 88.83 nm RMS surface topography

18 obtained on the same single crystal silicon substrate by deposition of a layer of nano-

19 particles from a reactive vapor phase comprising TMA and water vapor. Rather than one

20 deposition cycle, 15 deposition cycles were used, where the amount of TMA and water

21 vapor present were decreased and the reaction time was decreased from that used to

22 produce the nano-particles layer shown in Figure 1.

23 [0049]   Figure 4 shows an AFM image of a 124 nm RMS surface topography obtained

1   on the same single crystal silicon substrate by deposition of a layer of nano-particles from

2   a reactive vapor phase comprising TMA, water vapor, and perfluorodecyltrichlorosilane

3   (FDTS).

4   [0050]   Figures 5A - 5D show a series of photos of a water droplet being dragged

5   along a super-hydrophobic surface of the kind created using the method of the present

6   invention. Since the surface cannot be made wet, it is almost impossible to deposit the

7   droplet onto such a surface. The droplet is repelled so strongly that it bounces off.

8   [0051]   Figure 6A shows the surface of a mini I-Pod ® board after corrosion by an

9   accidental Gatorade® spill over the surface of an I-Pod.

10   [0052]   Figure 6B shows the back of the control click wheel of the mini I-pod after the

11   accidental Gatorade® spill referred to with respect to Figure 6A.

12   [0053]   Figure 7 A shows a cell phone board which was unprotected and exposed to

13   water for a time period of about 10 minutes at atmospheric pressure and ambient

14   temperature conditions. Wetting, which can lead to corrosion is evident in the central

15   portion of the board.

16   [0054]   Figure 7B shows the same model of cell phone board which was protected

17   with a super-hydrophobic film of the kind described herein and exposed to water for a

18   time period of about 10 minutes at atmospheric pressure and ambient temperature

19   conditions. No wetting of the board was observed after the exposure.

20   [0055]   Figure 8 shows a flash memory board of the kind which was tested for

21   protection from liquids by a super-hydrophobic film of the kind described herein.

1   [0056]   **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

2   [0057]   One aspect of the present invention relates to a chemical vapor deposition

3   method of coating and treating materials to provide super-hydrophilic and/or super-

4   hydrophobic surface properties. In a method embodiment of the invention, a rough

5   surface is created using the CVD deposition of particles formed *in situ* in the gas phase

6   above a substrate. The method includes: Reacting two or more vaporous precursors in

7   the gas phase under vacuum at sub-atmospheric pressures to form nano-particles. The

8   nano-particles are subsequently deposited on the substrate, forming a rough surface

9   texture. The gas phase reaction parameters are controlled so that the size of the nano-

10   particles formed in the gas phase is on the order of tens-to-hundreds of nanometers.

11   Typically the processing parameters which are controlled include the amount of reactants,

12   the relative amount of reactants, reaction pressure, time, and temperature during the CVD

13   reaction. A number of CVD deposition cycles may be used, with the number of cycles

14   affecting the size of the nano-particles. The topography which results on the surface of a

15   substrate on which the nano-particles have been deposited can be detected using AFM

16   (Atomic Force Microscopy) by way of example, and not by way of limitation. This

17   measurement technique provides an image of the surface and permits calculation of

18   various feature sizes, including a surface roughness in nm RMS (Random Mean Square)

19   which permits an overall comparison of various surface roughness from sample to sample

20   evaluated.

21   [0058]   A super-hydrophilic surface typically exhibits a contact angle of 0 degrees, and

22   is obtained when the nano-particles formed in the CVD reaction are hydrophilic particles.

23   A super-hydrophilic surface can subsequently be made super-hydrophobic by deposition

24   of a hydrophobic self-aligned monolayer (SAM), which may be applied by vapor

25   deposition or any other conventional deposition method including deposition from liquid.

26   Alternatively, a super-hydrophobic surface may be obtained when the nano-particles

27   formed in the CVD reaction are hydrophobic particles.

1   [0059]   As previously described, a super-hydrophobic surface typically exhibits a

2   contact angle which is greater than about 150 degrees. A super-hydrophobic surface

3   obtained by one of the above reactions can subsequently be tailored to a desired degree of

4   hydrophobicity or may be converted to completely exhibit super-hydrophilic properties in

5   desired areas by removing the hydrophobic film from the substrate surface by means of

6   etching or radiation exposure. Masking or patterning by using lithographic techniques

7   can be used to create patterns and gradients of super-hydrophobic and super-hydrophilic

8   areas.

9   [0060]   A rough super-hydrophilic surface which has been patterned as described

10   above can be subsequently functionalized to provide a desired surface reactivity for a

11   particular chemistry using standard silanization methods in either vapor or liquid phase.

12   [0061]   EXAMPLES OF CHEMICAL VAPOR DEPOSITION OF
13   SUPER-HYDROPHOBIC OR SUPER HYDROPHILIC SURFACES

14   [0062]   Example One:

15   [0063]   During current experimentation, we formed rough alumina films in a single

16   step by nucleating alumina nano-particles in a gas phase and depositing them onto a

17   single crystal silicon substrate. In one implementation a CVD reaction of TMA

18   (trimethylaluminum) and water vapor was used. In the past, such spontaneous gas phase

19   reactions were considered to be problematic since they produced undesirable particles due

20   to gas phase nucleation. In the present instance, such a gas phase reaction has been

21   purposely used to form nano-particles. The reaction parameters are selected to control the

22   rate of nano-particle formation and consequently the desired size of the surface roughness

23   features. Examples of the reaction parameters and their impact on surface roughness are

24   shown in the Table One below, where reaction precursors of TMA and Water Vapor were

25   used to produce roughened surfaces. In one instance, a combination of TMA, Water

26   Vapor and perfluorodecyltrichlorosilane (FDTS) reaction precursors were used to produce

1   a particularly rough surface.

2   **[0064]**   The chemical vapor deposition reactions described below were carried out

3   using an MVD-100 processing system which is commercially available from Applied

4   Microstructures, Inc. of San Jose, California.

5   **[0065]**   TABLE ONE

Run No.	FDTS Partial Pressure (Torr)*	TMA Partial Pressure (Torr)*	H₂O Vapor Partial Pressure (Torr)*	Time (min)	Temp (°C)	Layer Thickness Å	RMS (nm)
1	--	6	40	10	60	___	8.5
2	--	7	40	10	60	___	13.3
3	--	4	30	0.5	60	___	88.8
4	4 x 0.5 **	1	40	1	60	___	123.6

12   * The reactant was measured by placement in a known volume at the pressure indicated
13   and that amount of material was charged to the CVD chamber. Therefore, the relative
14   amounts of each of the reactants is indicated by its partial pressure in Torr.
15   ** The FDTS exhibits a lower vapor pressure, and four volumes of material, each
16   volume at 0.5 Torr were charged to the CVD chamber over a time period of about 10
17   seconds. The reaction time periods referred to above indicate the reaction time after all of
18   the reactants have been injected.

19   **[0066]**   While perfluorodecyltrichlorosilane (FDTS) is used in the example above,

20   there are a number of other silanes which may be used. Other example materials include,

21   but are not limited to fluoro-tetrahydrooctyldimethylchlorosilane (FOTS),

22   undecenyltrichlorosilanes (UTS), vinyl-trichlorosilanes (VTS), decyltrichlorosilanes

23   (DTS), octadecyltrichlorosilanes (OTS), dimethyldichlorosilanes (DDMS),

24   dodecenyltricholrosilanes (DDTS), perfiuorooctyldimethylchlorosilanes,

25   aminopropylmethoxysilanes (APTMS), fluoropropylmethyldichlorosilanes, and

26   perfluorodecyldimethylchlorosilanes.   The OTS, DTS, UTS, VTS, DDTS, FOTS, and

1   FDTS are all trichlorosilane precursors. The other end of the precursor chain is a

2   saturated hydrocarbon with respect to OTS, DTS, and UTS; contains a vinyl functional

3   group, with respect to VTS and DDTS; and contains fluorine atoms with respect to FDTS

4   (which also has fluorine atoms along the majority of the chain length). One skilled in the

5   art of organic chemistry can see that the vapor deposited coatings from these precursors

6   can be tailored to provide particular functional characteristics for a coated surface. The

7   use of precursors which provide a fluorocarbon or a hydrocarbon surface provide

8   excellent hydrophobic properties.

9   [0067]   As previously mentioned, adding an organo-silane fluorocarbon reactant to the

10   process in which the nano-particles are formed may be used as a method of obtaining a

11   surface which exhibits hydrophobic or functional properties. In the alternative, an

12   organo-silane may be used for formation of a thin film over the surface of the deposited

13   nano-particles.   Organo-silane precursor materials may include functional groups such

14   that the silane precursor includes an alkyl group, an alkoxyl group, an alkyl substituted

15   group containing fluorine, an alkoxyl substituted group containing fluorine, a vinyl group,

16   an ethynyl group, or a substituted group containing a silicon atom or an oxygen atom, by

17   way of example and not by way of limitation.   In particular, organic-containing precursor

18   materials such as (and not by way of limitation) silanes, chlorosilanes, fluorosilanes,

19   methoxy silanes, alkyl silanes, amino silanes, epoxy silanes, glycoxy silanes, and

20   acrylosilanes are useful in general.

21   [0068]   Figure 1 shows an AFM image of the 8.53 nm RMS surface topography

22   obtained on a single crystal silicon substrate by deposition of a layer of nano-particles

23   from a reactive vapor phase comprising trimethyl aluminum (TMA) and water vapor

24   using the processing conditions specified under Run No. 1 in the Table One above.

25   [0069]   Figure 2 shows an AFM image of a 13.3 nm RMS surface topography

26   obtained on the same single crystal silicon substrate by deposition of a layer of nano-

27   particles from a reactive vapor phase comprising TMA and water vapor using the

1   processing conditions specified under Run No. 2 in Table One above.

2   [0070]   Figure 3 shows an AFM image of an 88.83 nm RMS surface topography

3   obtained on the same single crystal silicon substrate by deposition of a layer of nano-

4   particles from a reactive vapor phase comprising TMA and water vapor using the

5   processing conditions specified under Run No. 3 in Table One above.

6   [0071]   Figure 4 shows an AFM image of a 124 nm RMS surface topography obtained

7   on the same single crystal silicon substrate by co-deposition of a layer of nano-particles

8   from a reactive vapor phase comprising TMA, water vapor, and (FDTS) using the

9   processing conditions specified under Run No. 4 in Table One above.

10   [0072]   As can be seen, large variation of surface roughness can be achieved as a

11   function of the processing conditions. In the case of insufficient gas phase reaction the

12   resulting surface roughness is too small (RJvIS < 5 nm) and the contact angle is degraded.

13   Uncontrollable gas phase reactions result in formation of boulders and agglomerates with

14   surface features that are too large (RMS > 100) and typically unstable.

15   [0073]   When the partial pressure of TMA was 1 Torr, the partial pressure of water

16   vapor was 40 Torr, and the partial pressure of FDTS was 2.0 Torr, as shown in Table One,

17   this set of conditions produced a topographic layer where the surface roughness was about

18   124 nm RMS, and the layer was fluffy and did not provide good adhesion to the substrate.

19   The roughness of the resulting super-hydrophobic coating is shown in Figure 4. The AFM

20   roughness image of the super-hydrophobic layer indicates a thickness of 15OA; RMS

21   greater than 123 nm; grey areas with light borders indicate peaks (the largest size features

22   on the surface); dark image color indicates valleys. Larger freatures appear to be made out

23   of smaller size particles (see shaded contours) which are visibly distributed across the

24   surface.

25   [0074]   By adjusting the partial pressure of these reactants to fall within the range

26   specified below, in Example Two, better control over the topographic layer produced was

27   obtained, and the surface roughness decreased to fall within a range of about 8 nm RMS to

1   about 20 nm RMS. The topographic layer produced was not fluffy and exhibited improved

2   adhesion based on a wiping test.

3   **[0075]**   Example Two:

4   **[0076]**   As discussed above, a single step reaction can be used to form a super-

5   hydrophobic film. A one-step CVD reaction may be carried out, which consists of

6   introducing two highly reactive vapors (TMA and Water) and a fluorocarbon vapor

7   (FDTS) into the reactor under controlled conditions to form hydrophobic nano-particles,

8   and depositing the resulting nano-particles onto a substrate surface to form a super-

9   hydrophobic topographic layer having a water contact angle >150 degrees. It was

10   necessary to adjust the relative precursor partial pressures which were illustrated in Run

11   No. 4 of Table One to obtain a topographic layer which showed lower porosity and better

12   adhesion to the substrate. Recommended reaction precursors and process conditions are as

13   follows: TMA, partial pressure 0.2-2 Torr; Water vapor, partial pressure 2-20 Torr; FDTS,

14   partial pressure, 0.02-0.5 Torr; Reaction temperature, room temperature to 100 ^{0}C,

15   typically 40-70 ^{0}C; Reaction time 5-30 min. This reaction can be repeated for a number of

16   cycles depending on requirement of thickness of the topographic layer produced and the

17   roughness characteristics of the substrate surface created. Typically a surface roughness in

18   the range of about 10 nm RMS to about 80 nm RMS is indicative of an acceptable

19   hydrophobic topographic layer.

20   **[0077]**   Precursors other than TMA and water, e.g. metal chlorides or highly reactive

21   chlorosilanes, can be used alternatively to produce similarly rough surface topography.

22   **[0078]**   In case of substrate materials which are difficult to adhere to (polymers,

23   plastics, certain metals, etc.), conventional metal oxides, silicon oxides, nitride films or

24   organic layers can be deposited as adhesion layers prior to roughening of the surface to

25   become super-hydrophilic or super-hydrophobic. As an example, we have used a low

26   temperature atomic layer deposition (ALD) reaction using TMA and water vapor to form

1   the adhesion layer. Such a reaction is well known in the literature and consists of

2   alternating exposure of the substrate to TMA (step A) and water (step B) in a number of

3   repetitive AB cycles, a method conceptually different than the reaction described above for

4   the creation of nano-particles. The use of the same reactants for both adhesion layer as

5   well as the rough top layer is, however, very beneficial as it allows the use of a single

6   CVD/ALD reactor for film deposition.

7   [0079]   Example Three:

8   [0080]   A two step reaction may be used to produce a super-hydrophobic film. In this

9   example, a two step CVD reaction was carried out, comprising:

10   Step 1) Introducing two highly reactive vapors (TMA and Water) into the

11 reactor under controlled conditions (below) to form hydrophilic nano-particles and

12 depositing the resulting nano-particles onto a substrate surface, followed by

13   Step 2) Functionalizing the resulting rough surface with a hydrophobic coating

14 by vapor deposition of a SAM (FDTS, perfiuorodecyltrichlorosilane, precursor was used,

15 for example and not by way of limitation).

16 [0081]   Preferred reaction precursors and CVD process conditions for the two step

17 reaction: Step 1): TMA, partial pressure 2 - 10 Torr; Water, partial pressure 20-60 Torr;

18 Reaction temperature, room temperature to 100 ^{0}C, typically 40-70 ^{0}C; Reaction time 5-30

19 minutes. Step 2): FDTS, partial pressure 1 - 2 Torr; Water, partial pressure 5 - 10 Torr;

20 Reaction temperature, room temperature to 100 °C; typically 40-70 °C; Reaction time 5-15

21 minutes.

22 [0082]   The first step can be repeated a number of cycle times depending on the

23 requirement of thickness of the topography layer produced and the roughness

24 characteristics of the substrate surface created.

25 [0083]   The results after each step were monitored and determined to be as follows. A

26 Super-hydrophilic surface was obtained after Stepl, where the water contact angle was 0

1   degrees, and there was complete wetting, so no sliding angle is measurable. A Super-

2   hydrophobic surface was obtained after Step 2, where the water contact angle was >150

3   degrees, and the sliding angle was <5 deg.

4   [0084]   A typical super-hydrophobic surface obtained using the two step process

5   exhibits a surface roughness ranging between about 8 nm RMS and about 20 nm RMS,

6   similar to the surface roughness obtained using the single step process described in

7   Example Two. The adhesion to the underlying single crystal silicon substrate was also

8   similar to that obtained using the single step process described in Example Two.

9   [0085]   The wetting behavior and repelling of water which occurs on a super-

10   hydrophobic surface of the kind described herein is illustrated in Figures 5A - 5D. Figures

11   5A - 5D are a series of photographs which show a water droplet being dragged along the

12   super-hydrophobic surface. Since the surface cannot be made wet, it is almost impossible

13   to deposit the droplet onto such a surface. The water tends to jump off the surface onto an

14   area surrounding the sample.

15   [0086]   Example Four:

16   [0087]   A super-hydrophobic film with an in-situ adhesion/barrier layer can be

17   produced using one embodiment of the method. In the case of materials which exhibit

18   poor adhesion (polymers, plastics, certain metals, etc.) conventional Spin-on, PVD, CVD,

19   or ALD metal oxides, silicon oxides, as well as the corresponding nitride films can be

20   deposited as adhesion layers prior to creation of a super-hydrophobic film. In the present

21   example we have used the same reactants for both the adhesion layer as well as the super-

22   hydrophilic top layer to allow the use of a single reactor and an in-situ deposition of the

23   multilayer film. Specifically, an ALD reaction of TMA and water was used to form an

24   ALD alumina adhesionftarrier layer. The reaction consists of alternating exposure of the

25   substrate to reactants A and B in a number of repetitive AB cycles with a nitrogen gas

26   purge and pump steps in between each A and B step, to remove the residual non-adsorbed,

1   non-reacted chemicals - a method conceptually different than the reaction described above

2   for the creation of nano-particles.

3   **[0088]**   Step 1) Deposition of an ALD adhesion/barrier layer: Sequentially injecting

4   TMA and water vapor precursors into the reactor to form 20- 300 A thick layer of ALD

5   alumina. Process conditions: Precursor A (TMA), partial pressure 0.2-2 Torr ; Precursor B

6   (Water), partial pressure 2-20 Torr; Reaction temperature 20 - 150 °C (typically 40-70

7   °C); Number of repetitions of step A followed by step B (a cycle): 30-100 with nitrogen

8   purge/pump in-between injections of precursor A and precursor B.

9   **[0089]**   Step 2) Deposition of super-hydrophobic layer by either of the methods

10   described in Examples 2 and 3.

11   **[0090]**   The super-hydrophobic surface properties were essentially the same as those

12   described for Examples 2 and 3.

13   **[0091]**   Example Five:

14   **[0092]**   A super-hydrophobic surface of the kind described above can subsequently be

15   tailored to a desired degree of hydrophobicity or can be patterned to exhibit super-

16   hydrophilic properties in selected areas by selectively removing the hydrophobic coating

17   from the surface. Masking or patterning by using lithographic techniques can be used,

18   combined with oxygen etching or U.V. Exposure.

19   **[0093]**   A super-hydrophobic film surface was exposed through a shadow mask to 254

20   nm/185 run UV radiation in air, sample distance from the UV source was 6 mm, allowing

21   for a selective removal of the hydrophobic properties in areas illuminated by UV radiation.

22   A similar result could be obtained by lithographic patterning and plasma etching of the

23   film. As can be seen in Table Two, forming a pattern of super-hydrophobic and super-

24   hydrophilic areas is feasible.

25   **[0094]**   The contact angle was measured in various areas of a patterned structure, where

26   portions of the structure were exposed to U.V. radiation.

1   [0095]   TABLE TWO

2	EXPOSURE TIME	5 MINUTES
3 4	Contact angle in UV exposed area (line of sight)	<3 (Super-hydrophilic) (complete removal)
5 6	Contact angle under the shadow mask (not exposed to UV light)	>150 (Super-hydrophobic) (zero removal)

7   [0096]   Another aspect of the present invention relates to use of the super-hydrophobic

8   and super hydrophilic surfaces in product applications. One of the major applications for

9   the super-hydrophobic surfaces pertains to protecting objects such as boards and

10   components of electronic devices from damage due to accidental and environmental factors,

11   especially due to wetting, spills and water condensation. Another of the major applications

12   for the super-hydrophilic surfaces is in the field of biotechnology, where diagnostic tools

13   and bio-compatible implants, for example find a super-hydrophilic biocompatible surface to

14   be advantageous.

15   [0097]   Application embodiments related to the protection of electronic boards and

16   components of electronic devices is illustrated below. Electronic devices of particular

17   vulnerability include digital cameras, cell phones, digital music and video players, portable

18   computers, marine electronics and other devices that require continuous operation in

19   adverse weather conditions and resistance to occasional exposure to water or liquids. A

20   protective coating typically includes a combination of a single or muti-layer inorganic

21   moisture barrier films followed by deposition of a super-hydrophobic film using the present

22   method. The inorganic films can be either metal oxide or metal nitride films grown using

23   conventional ALD or PVD techniques. Specifically, alumina (A12O3) and titania (Ti2O5)

24   films and their multi-layer combinations are well suited for moisture and gas permeability

25   protection. TMA and TiC14 (titanium tetrachloride) precursors were used respectively for

26   depositing alumina and/or titania films with water vapor in an ALD reaction. The top layer

1   of super-hydrophobic film was grown using the methods referenced above.

2   [0098]   Experimentation has been carried out by forming various protective film

3   combinations on electronic boards of cell phones, i-Pods, and flash cards. Electronic device

4   boards were removed from the respective electronics products and coated with a dual layer

5   film. The first layer of ALD alumina was IOOA thick. The second super-hydrophobic layer

6   was grown in-situ using TMA, water, and FDTS. Coated, reassembled, and electrically

7   powered boards were subjected to accelerated tests by immersion in a highly ionized water

8   solution. Unprotected electronic boards or electronic devices immersed in such corrosive

9   ionic solution typically fail in a catastrophic way within the first 1-2 seconds of immersion.

10   Protected boards continued working for at least the 10 minute time period during which

11   they were tested.

12   [0099]   Example Six:

13   [0100]   An i-Pod Shuffle, Mini i-Pod board was found to corrode as a result of an

14   accidental soft drink spill (Figures 6A and 6B). Subsequently, coated I-Pod Shuffle units

15   were tested for protection against such spills. The I-Pod Shuffle was turned on (playing

16   music) and then immersed in a highly concentrated Gatorade® solution of sodium and

17   potassium ions. The unprotected I-Pod stopped operating within seconds. The I-Pod

18   protected by the super-hydrophobic coating continued to operate for up to ten minutes while

19   immersed in the test bath. The i-Pod was then rinsed with water, dried, and remains fully

20   operational after several weeks. The Figure 6A and 6B photos show the damage to the

21   main board, and to the back of the control click wheel, respectively. There is evidence of

22   extreme corrosion and the unit is beyond repair. Application of the super-hydrophobic layer

23   over the surface of the Mini i-Pod helps reduce the possibility of such damage, and enables

24   salvaging of the electronic device in most instances.

1   [0101]   Example Seven:

2   [0102]   Mobile phone board assemblies, illustrated in Figure 7, were removed from the

3   phone plastic housing and coated with an alumina/super-hydrophobic coating. The entire

4   boards were then immersed in tap water for a time period of about 10 minutes, and were

5   shown to be protected from water, which would immediately spill off. Re-assembled

6   phones tested for functionality were found to be fully operational and resistant to wetting.

7   [0103]   A cell phone board 702 illustrated in Figure 7, which was uncoated, wets well

8   and accumulates moisture. A cell phone board 704, which was coated with the

9   alumina/super-hydrophobic dual layer previously described, does not wet and resists

10   moisture accumulation. Both boards look similar, as the protective coating is transparent to

11   visible light; however, the coated board does not wet. Digital cameras and other

12   electronics protected by such a metal oxide (or metal nitride)/super-hydrophobic dual layer

13   will be protected in a manner similar to that described with respect to the mobile phone

14   board assemblies. Protective coatings described above can be used in many other

15   electronics products including but not limited to computer boards, keyboards, electronic

16   games, and GPS devices can be protected. An entire board of a Blackberry device coated

17   with a protective anti-wetting film was soaked in red ink solution for a time period of about

18   10 minutes, and then rinsed in water and dried. The Blackberry device was then re-

19   assembled and has since been in continuous use. Although tests using digital cameras were

20   not performed in this study the inventors contend there is a high degree of certainty that the

21   alumina/super-hydrophobic coating would have a similar protective effect when used to

22   protect digital cameras.

23   [0104]   Example Eight:

24   [0105]   A Flash Memory Stick of the kind shown in Figure 8 was connected to the

25   computer via USB port and immersed in the test bath. Access to the files stored in the flash

26   memory was tested as a function of time. An unprotected flash memory board stopped

1   operating in an ionic liquid immersion test within the first two seconds. A protected flash

2   memory board coated with a thin (100A) layer of ALD alumina film exhibited similar

3   failure of operation within 2 seconds of immersion. However, with the ALD alumina film

4   present, the operation could be recovered by rinsing the board with water and drying. To

5   our surprise, a similar result was obtained in the case of a dual layer protective coating,

6   where the dual layer consisting of an ALD alumina underlayer, with a CVD layer of a SAM

7   fluorocarbon film. Immediate failure occurs despite the fact that the SAM fluorocarbon

8   film provides an additional anti-wetting protection. The alumina/super-hydrophobic dual

9   layer coating was found to provide the highest degree of protection. This dual layer coating

10   enables continuous operation of the memory board immersed in the test bath for over 10

11   minutes. This is due to the ability of the super-hydrophobic film to protect the underlying

12   alumina from the test liquid. Moreover, the board can easily be rinsed in water and dried

13   after the test without any damage to its operation. The re-assembled device remains fully

14   functional after several weeks of operation.

15   [0106]   Example Nine:

16   A single crystal silicon wafer was coated with a super-hydrophobic layer in the

17   manner described in Example Three. The surface of the coated wafer was then exposed to

18   patterned U.V. radiation through a mask using a UV-Ozone system of the kind available

19   from UVOCS Corporation of Montgomeryville, Pennsylvania. The pattern was one of

20   microfluidic channels of the kind which are used for diagnostics in the medical industry.

21   The super-hydrophobic layer was removed (stripped away) from areas which were exposed

22   to UV in the presence of Ozone. The resultant device was an array of microfluidic

23   channels, which were created without the need to etch a substrate surface.

24   [0107]   The above described exemplary embodiments are not intended to limit the scope

25   of the present invention, as one skilled in the art can, in view of the present disclosure

1   expand such embodiments to correspond with the subject matter of the invention claimed

2   below.

[0108]   CLAIMS

[0109]   We claim:

1.   A chemical vapor deposition method of forming a layer upon a surface of a substrate, which layer provides a topography over said substrate surface which can be tailored to provide a super-hydrophobic property or a super-hydrophilic property, wherein the topography which enables the super-hydrophobic or super-hydrophilic property is created by controlling chemical vapor deposition process parameters, including the chemical composition of the reactants, the relative amounts of the reactants, the process pressure, the process temperature, and the reaction time, such that nano-particles are produced in a vapor phase over the substrate surface and are deposited on said substrate surface in a controlled manner, to produce a surface topography which exhibits said super-hydrophobic or said super-hydrophilic property.

2.   A chemical vapor deposition method in accordance with Claim 1, wherein an RMS surface roughness ranging between about 8 nm RMS to about 100 nm RMS is obtained.

3.   A method in accordance with Claim 1, in which said chemical reactants used to form a topographic layer over said substrate surface comprise water vapor and at least one additional chemical reactant selected from the group consisting of an organometallic compound, a metal chloride, a silane compound and combinations thereof.

4.   A method in accordance with Claim 3, in which wherein said chemical reactants used to form a topographic layer over said substrate surface comprise an organometallic compound.

1   5.   A method in accordance with Claim 4, wherein the metal present in said

2   organometallic compound is selected from the group consisting of aluminum, titanium, and

3   combinations thereof.

1   6.   A method in accordance with Claim 5, wherein said organometallic compound

2   is tiimethyl aluminum.

1   7.   A method in accordance with Claim 3, wherein said at least one chemical

2   reactant is a metal chloride or a silicon chloride selected from the group consisting of

3   aluminum trichloride, titanium tetrachloride, silicon tetrachloride and combinations thereof.

1   8.   A method in accordance with Claim 3, wherein said at least one chemical

2   reactant is a silane compound selected from the group consisting of a chlorosilane, an

3   amino silane, and combinations thereof.

1   9.   A method in accordance with Claim 8, wherein said at least one chemical

2   reactant is a reactive chlorosilane selected from the group consisting of

3   perfluorodecyltrichlorosilane (FDTS), fluoro-tetrahydrooctyldimethylchlorosilane (FOTS),

4   undecenyltrichlorosilanes (UTS), vinyl-trichlorosilanes (VTS), decyltrichlorosilanes (DTS),

5   octadecyltrichlorosilanes (OTS), dimethyldichlorosilanes (DDMS),

6   dodecenyltricholrosilanes (DDTS), perfluorooctyldimethylchlorosilanes,

7   aminopropylmethoxysilanes (APTMS), fluoropropylmethyldichlorosilanes, and

8   perfluorodecyldimethylchlorosilanes and combinations thereof.

1   10.   A method in accordance with Claim 2, or Claim 3, wherein a substrate surface

2   exhibiting a super-hydrophilic property is formed.

11.   A method in accordance with Claim 10 wherein, subsequent to formation of said super-hydrophilic surface, a functionalizing layer is deposited over said super-hydrophilic surface to create a super-hydrophobic surface.

12.   A method in accordance with Claim 11, wherein said subsequently deposited functionalizing layer is deposited using chemical vapor deposition.

13.   A method in accordance with Claim 12, wherein said functionalizing layer is deposited in a processing chamber in which said super-hydrophilic surface layer was deposited.

14.   A method in accordance with Claim 3, wherein a hydrophobic chemical reactant is added to said chemical reactants at a time said nano-particles are formed.

15.   A method in accordance with Claim 1, wherein a surface with a super-hydrophobic property is formed, and wherein said super-hydrophobic surface is partially converted to a super-hydrophilic surface, in the form of a pattern by means of selective exposure to UV-oxygen or plasma etching of said super-hydrophobic surface.

16.   A method in accordance with Claim 1, wherein a surface with a super-hydrophilic property is formed, wherein subsequently a functionalizing layer is deposited over said surface having said super-hydrophilic property to provide a surface with a super-hydrophobic property, and wherein said super-hydrophobic surface is partially converted to a super-hydrophilic surface, in the form of a pattern by means of selective exposure to UV-oxygen or plasma etching of said super-hydrophobic surface.

1   17.   A method in accordance with Claim 1 or Claim 3, wherein a plurality of
2   chemical vapor depositions are made in sequence to provide a layer having a desired
3   nominal thickness and surface roughness.

1   18.   A method in accordance with Claim 1, wherein, subsequent to formation of said
2   super-hydrophobic surface, a functionalizing layer is deposited over said super-hydrophobic
3   surface which creates a super-hydrophilic surface.

1   19.   A method in accordance with Claim 1, wherein, subsequent to formation of said
2   super-hydrophilic surface, a functionalizing layer is deposited over said super-hydrophilic
3   surface which creates a super-hydrophobic surface.

1   20.   An article having at least one super-hydrophobic surface which was created in
2   accordance with the method of Claim 1 or Claim 19.

1   21.   An article having at least one super-hydrophobic surface which was created in
2   accordance with the method of Claim 14.

1   22.   An article having at least one super-hydrophilic surface which was created in
2   accordance with the method of Claim 1 or Claim 18.

1   23.   An article having at least one surface where a first portion of said surface
2   exhibits super-hydrophobic properties and where a second portion of said surface exhibits
3   super-hydrophilic properties, wherein said surface was created in accordance with the
4   method of Claim 15 or Claim 16.

1   24.   An article comprising an adhesion layer of silicon oxide or a metal oxide with a

2   surface layer applied directly over said layer of silicon oxide or metal oxide, wherein a first

3   portion of said surface layer exhibits super-hydrophobic properties, and a second portion of

4   said surface layer exhibits super-hydrophilic properties, wherein said surface layer was

5   created in accordance with the method of Claim 15 or Claim 16.

1   25.   A multilayer structure including a superhydrophobic film, said structure

2   comprising:

3   a) a layer made of organometallic nano-particles deposited by a vapor phase

4   reaction; and

5   b) a fluorocarbon or hydrocarbon layer overlying said layer made of

6   organometallic nano-particles.

1   26.   A multilayer structure in accordance with Claim 25, wherein said

2   superhydrophobic film exhibits a surface roughness ranging between about 8 run RMS and

3   about 100 nm RMS.

1   27.   A multilayer structure including a superhydrophilic film, said structure

2   comprising:

3   a) an oxide adhesion or passivation layer deposited upon a substrate surface;

4   b) a layer made of organometallic nano-particles deposited by a vapor phase

5   reaction, and overlying said oxide adhesion layer; and

6   c) a fluorocarbon or hydrocarbon layer overlying said layer made of

7   organometallic nano-particles.

1   28.   A multilayer structure in accordance with Claim 27, wherein said

2   superhydrophilic film exhibits a surface roughness ranging between about 8 nm RMS and
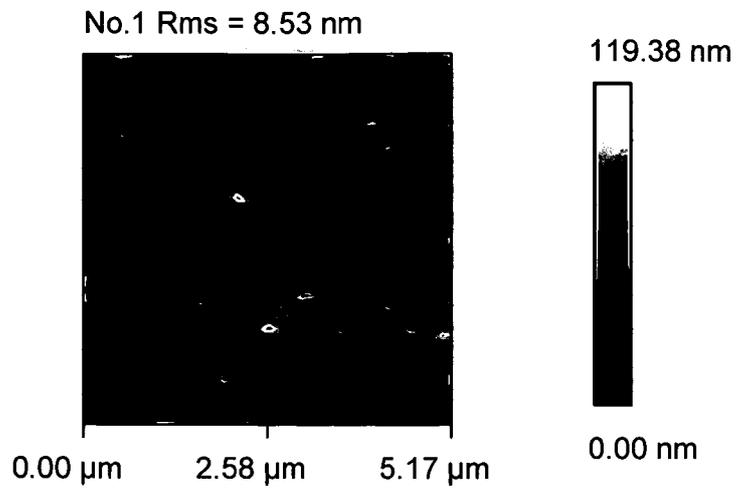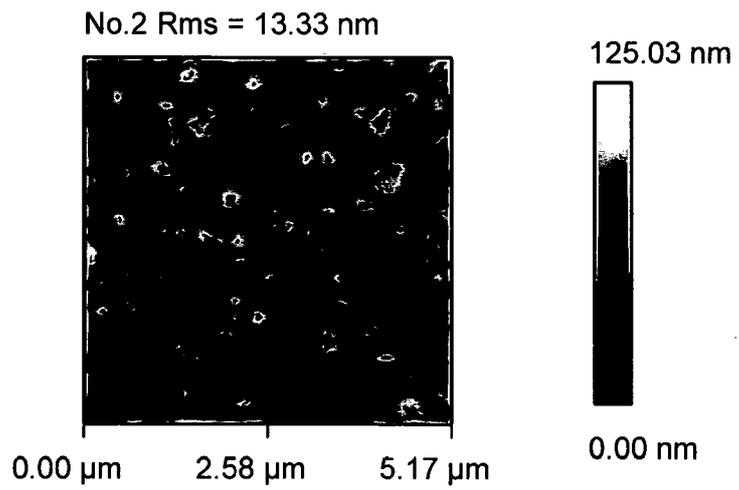
3   about 100 nm RMS.

1   29.   A multilayer structure comprising a superhydrophilic surface, said structure

2   comprising:

3   a) an oxide adhesion or passivation layer deposited upon a substrate surface;

4   b) a layer made of organometallic nano-particles deposited by a vapor phase

5   reaction and overlying said silicon oxide adhesion layer.

1   30.   A multilayer structure in accordance with Claim 29, wherein said

2   superhydrophilic film exhibits a surface roughness ranging between about 8 nm RMS and
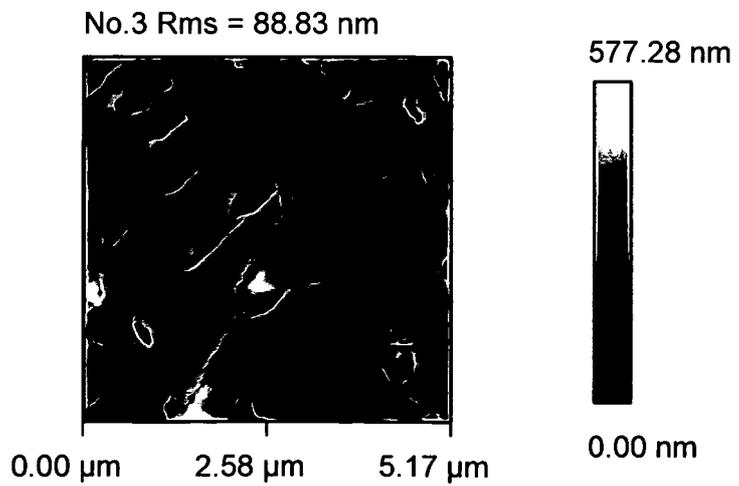
3   about 100 nm RMS.

No.1 Rms = 8.53 nm
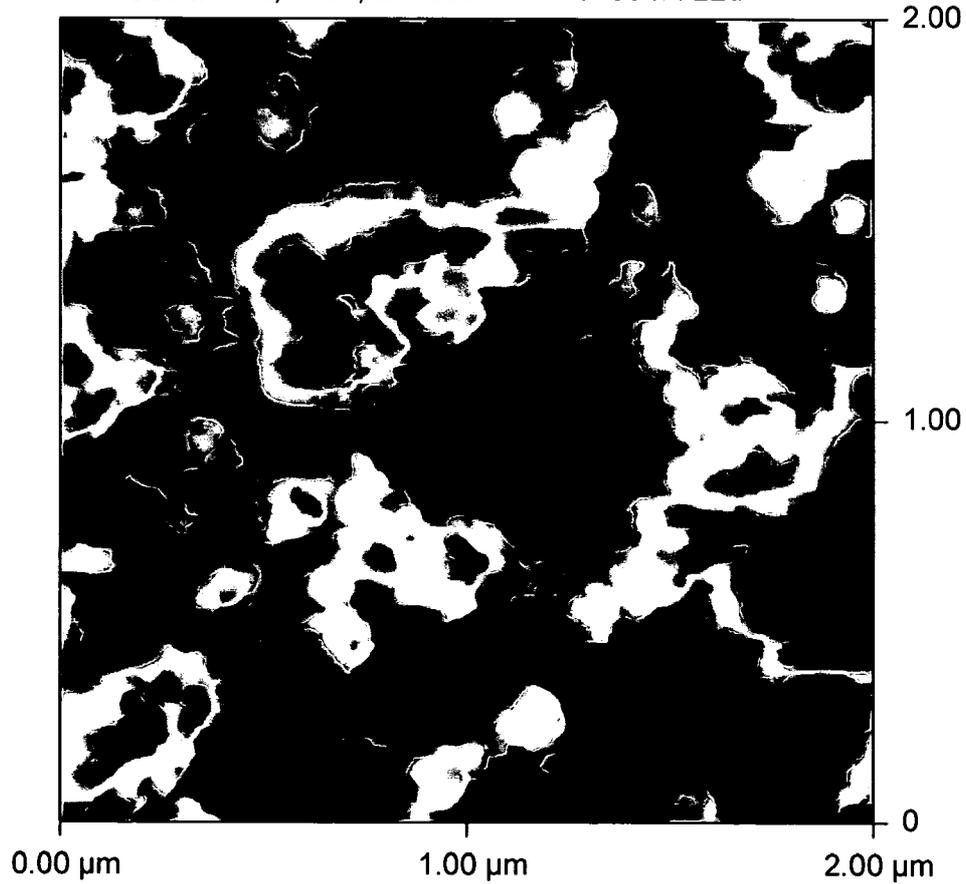
119.38 nm

Fig. 1

0.00 nm

0.00 μm   2.58 μm   5.17 μm

No.2 Rms = 13.33 nm

125.03 nm

Fig. 2

0.00 nm

0.00 μm   2.58 μm   5.17 μm

No.3 Rms = 88.83 nm

577.28 nm

Fig. 3

0.00 nm

0.00 μm   2.58 μm   5.17 μm

IMAGE STATISTICS	
Img. Rms (Rq)	123.62 nm
Img. Ra	97.562 nm
Img. Rmax	696.06 nm
Img. Srf. area	9.506 μm^2
Img. Srf. area diff	137.64 %

C06M4078, #164, Z = 500 nm м407864f . 22d

Fig. 4
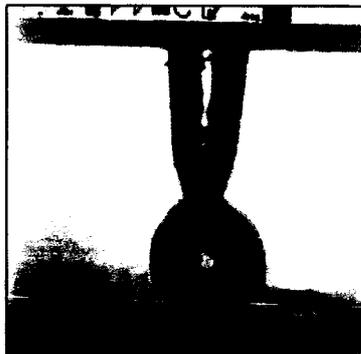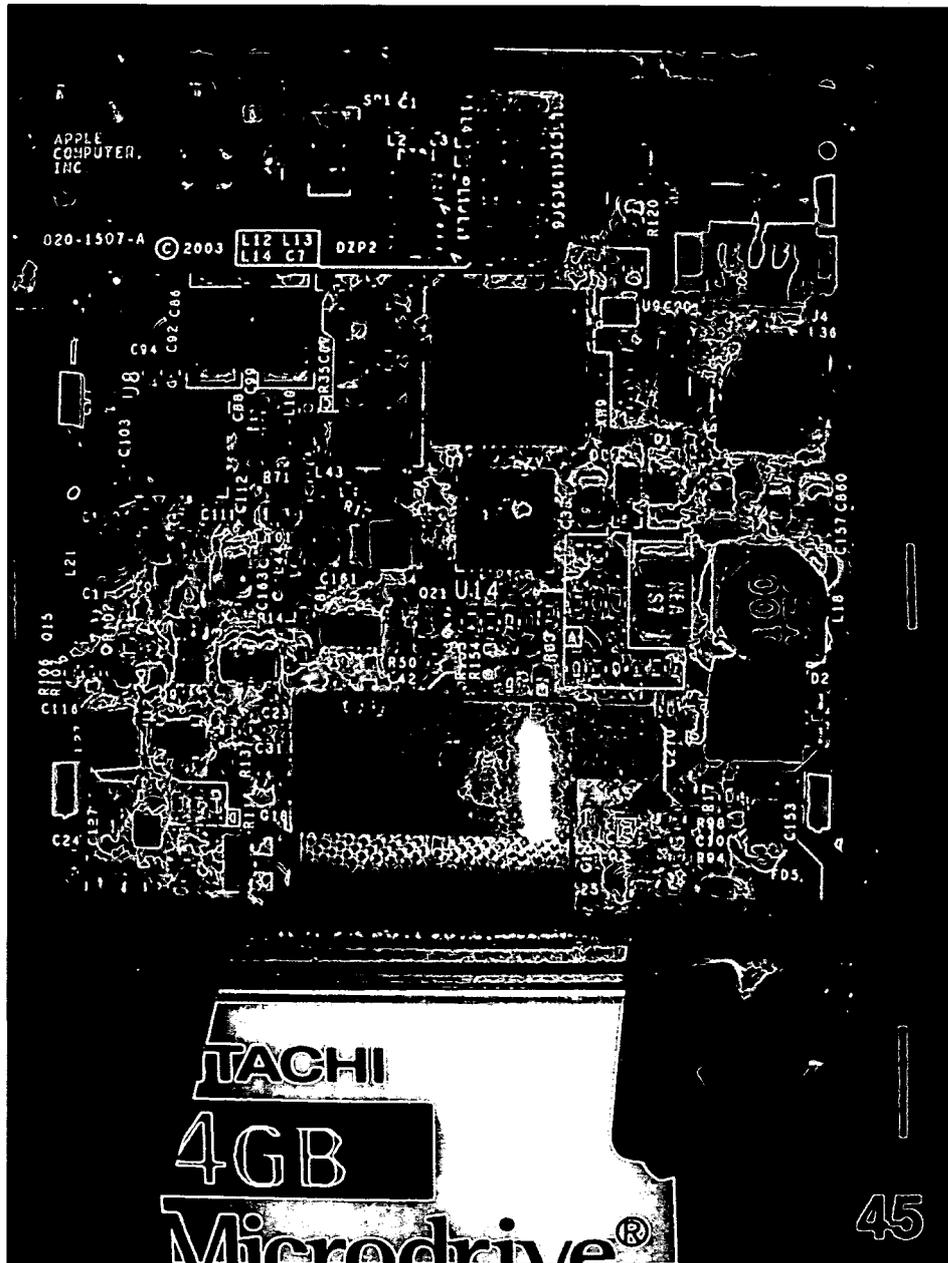
Fig. 5A

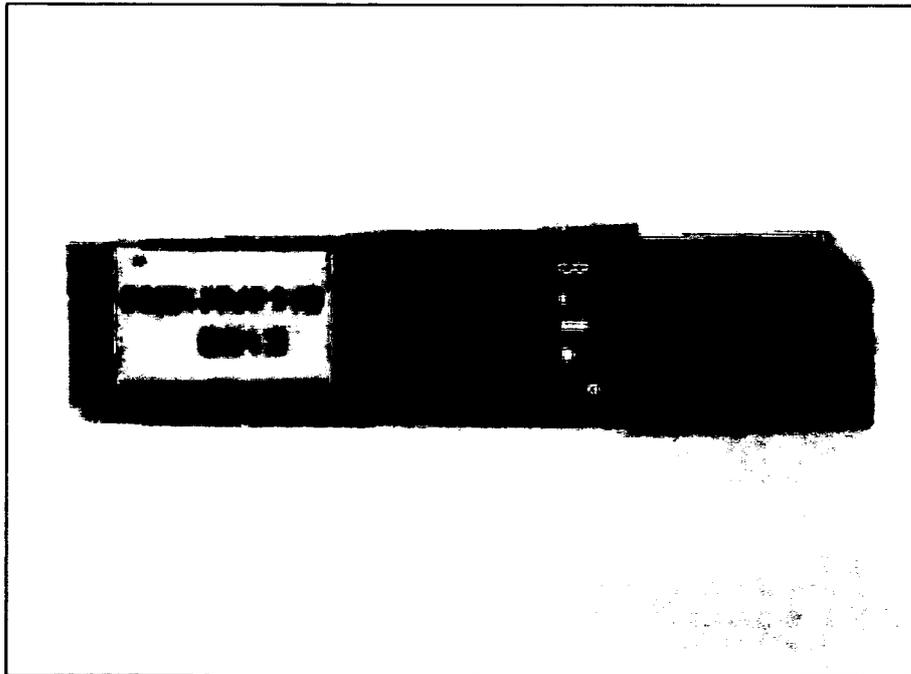Fig. 5B

Fig. 5C

Fig. 5D

Fig. 6A

5/6

Fig. 6B

704

702

Fig. 7

Fig. 8

INTERNATIONAL SEARCH REPORT

A CLASSIFICATION OF SUBJECT MATTER	

IPC(8) - B05D 3/02,   1/36 (2008.04)

USPC - 427/180

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)
USPC - 427/180

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 427/180,202,376 1,402, $
Search Terms Below

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (USPT, PGPB, EPAB, JPAB), google com
Search Terms Used   superhydrophobic,   super-hydrophilic,   water, vapor, layer, super, functionalizing,   CVD, aluminum,   trichloride,
tπmethyl, titanium, organometallic,   silane, amino

C   DOCUMENTS CONSIDERED   TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X -- Y	US 2005/0181 195 A 1 (Dubrow) 18 August 2005 (18 08 2005) entire document, especially Abstract, paras [0007], [0009], [0018], [0019], [0044], [0047], [0079], [0100], [0101], [01 13], [0127], [0129], [0134]	1-4, 8-10, 14-17, 20-30 ------------------------------- 5-7, 11-13, 18, 19
Y	US 6,475,910 B 1 (Sneh) 05 November 2002 (05 11 2002) entire document, especially Abstract, col 12, In 22-26	5-7
Y	US 2005/0219788 A 1 (Chow et al) 06 October 2005 (06 10 2005) entire document, especially Abstract, para [0058]	11-13, 18, 19

D Further documents are listed in the continuation of Box C	☐	

*   Special categories of cued documents
"A"   document defining the general state of the art which is not considered
      to be of particular relevance
"E"   earlier application or patent 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
04 June 2008 (04 06 2008)	**2 0 JUN** 2008
Name and mailing address of the ISA/US Mail Stop PCT, Attn ISA/US, Commissioner for Patents P O Box 1450, Alexand πa, Virginia 22313-1450 Facsimile No 571-273-3201	Authorized officer Lee W Young **PCT Helpdesk 571-272-4300** **PCT OSP 571 272 7774**

Form PCT/ISA/210 (second sheet) (April 2007)