(51) International Patent Classification:
G02B 1/10 (2006.01) C23C 16/40 (2006.01)

(21) International Application Number:
PCT/IB20 11/001791

(22) International Filing Date:
29 July 2011 (29.07.2011)

(25) Filing Language:
Italian

(26) Publication Language:
English

(30) Priority Data:
MI2010/001529 9 August 2010 (09.08.2010)


(72) Inventors; and

(75) Inventors/Applicants (for US only): DI MUNDO, Rosa [IT/IT]; c/o Universita degli Studi di Bari, Dipartimento di Chimica, Via Orabona, 4, 1-70126 Bari (BA) (IT). PALUMBO, Fabio [IT/IT]; c/o CNR-IMIP, Universita degli Studi di Bari, Dipartimento di Chimica, Via Orabona, 4, 1-70126 Bari (BA) (IT). D’AGOSTINO, Riccardo [IT/IT]; C/o Plasma Solution S.r.L., Via Orabona, 4, 1-70126 Bari (BA) (IT).

(74) Agent: GISLON, Gabriele; Marietti, Gislon e Trupiano S.r.L., Via Larga, 16, 1-20122 Milan (IT).


[Continued on next page]

(54) Title: OPTICAL ELEMENTS HAVING LONG-LASTING HYDROPHILIC AND ANTI-FOG PROPERTIES AND METHOD FOR THEIR PREPARATION

(57) Abstract: An optical element includes a body (6) made of transparent plastic material and at least one of the surfaces is modified in order to present a plurality of nanostructures (7) obtained directly onto the surface (5, 5') of the body (6); the nanostructured surface is at least partly coated with a film (15) of an hydrophilic material, preferably inorganic, and has superhydrophilic properties that are stable in time.

Published: with international search report (Art. 21(3))
“Optical elements having long-lasting hydrophilic and anti-fog properties and method for their preparation”.

Field of the invention

This invention relates to new plastic optical elements having permanent hydrophilic and anti-fog properties and to a method for their production. More in particular the invention concerns transparent plastic elements such as optical elements, but not exclusively, whose surface is treated to provide the same with hydrophilic and, therefore, anti-fog properties, and preferably also anti-reflective properties, that are stable and permanent in time. With the wording hydrophilic we want to define also the wording superhydrophilic and to define surfaces having properties corresponding to ACA angles within the range of 30° to 0° (zero degrees) as better explained hereinafter.

With optical elements and components we want here to define and cover various kinds of optical components in transparent plastic material (such as ophthalmic lenses, protective shields and visors, swimming goggles, ski masks, windows / showcases in plastic material, walls of refrigerated counters, windshield) whose visibility is reduced in fog conditions and whose performance must be improved. For the purposes of this description, transparent plastic material is intended to be made from plastic polymers such as e.g. polycarbonate, polymethylmethacrylate and polyolefins such as polyethylene terephthalate, polyethylene naphthalate, polystyrene, polyethylene, polypropylene or similar.

Background of the invention

The warm moist air condensing on a cold transparent surface, as is well known, results in fogging, that reduces visibility through the same surface, a fact inconvenient and sometimes even dangerous.

The fogging develops when the steam condenses on a surface not-sufficiently hydrophilic, i.e. a set of micro-droplets with a rounded shape is deposited on the surface, causing internal reflections in the light transmitted through the polymer material (see Figure 1).
Another problem with such optical components is the reflection of light on their surface reducing light transmission and producing unwanted glare. In the known art very different types of anti-fog modification of polymeric transparent surfaces are reported.

One method (which includes products such as Visgard®, Vistex®) consists in covering the surface of interest with a transparent film (typically polyethylene terephthalate, PET) with a thickness of about 100 μm layer, provided with an hydrophilic polymer top. This film, adhesive on one side, usually has to be applied by the consumer.

Another very common method consists in using chemical mixtures to be periodically applied on the surface of the optical component. If the object is small, it is dipped in the product. Alternatively, these products are applied as paints (eg. Chamelic). Examples of solutions of the type above described are shown in the following documents.


US5804612 (1998) refers to a polymer containing a hydroxyl group, a crosslinker containing aluminum, and a surface agent containing hydroxyl and/or siloxane groups.

US 5527854 (1996) proposes the use of an aqueous solution for treating hydrophilic surfaces using glutamic acid.

To overcome the problem of having to apply the above discussed polymeric "paints", alternative methods have been developed for modifying the structure of the surface of the transparent optical element. For example, in US5897925 (1999) a SiOH microporous film is obtained on the optical surface by a method which involves a thermal evaporation step; in US5487920 (1996) a process for the deposition of anti fog and anti scratch coatings via plasma is described for various substrates (deposition of a film containing silicon, and subsequent functionalization processing with N2O, CO2).

US 2010/0033819 (2010) provides the deposit on the optical material to be...
treated of a hydrophilic polymer with conventional methods and a subsequent treatment with plasma etching of the hydrophilic polymer layer to ultimately achieve an anti-fog effect and a simultaneous anti-reflecting effect.

The process described in that patent is complex and long to achieve, consisting in a number of steps with different technologies and reactors. In particular, the planned steps are: the deposition of a hydrophilic polymer layer (unclear technique, however, not based on plasma chemistry); deposition with another technique of a thin film of titanium dioxide as a catalyst for etching, etching with a plasma chemistry technique for nanostructuring; deposition with additional layers to improve the mechanical properties of the surface.

A further problem of the previously used anti-fog surfaces, as well as of the above discussed ones, is that their durability is reduced. In fact, as has long been known, see for example *F. Garbassi, M. Morra and E. Occhiello, Polymer Surfaces — From Physics to Technology, Wiley, San Diego, CA (1994)*, hydrophilic surfaces are inherently unstable in air and through a variety of phenomena the water contact angle tends to increase (within 2-3 weeks) thereby reducing or canceling the antifog effect.

Up to now, the known technique was not able to solve the problem of providing long lasting anti-fog properties to the treated surfaces when said surfaces are exposed to the ambient atmosphere.

It is an aim of the present invention to solve the above mentioned problem, to provide components or optical elements having an anti-fog layer that is effective and resistant, and to further provide a new simple and economic anti-fog treatment process for optical components.

**Summary of the invention**

This aim is achieved by means of the present invention concerning an optical component or element provided with an anti-fog layer, which is characterized according to claim 1.

The invention also concerns a method according to claim 9; said plasmochemical method for treating the surface of the optical elements includes the steps of (i) nanostructuring (forming a nanostructure on) the
surface of the optical elements using plasma etching and (ii) subsequent deposition of transparent hydrophilic film $\text{SiO}_x$ on the nanostructured surface. According to a preferred aspect of the invention, these steps are performed sequentially in the same reactor. Alternatively, they are carried out in different reactors.

This method gives the surface stable superhydrophilic character (with wetting in permeation regime) showing anti-fogging property. The superhydrophilic characteristic of the surface that has been treated according to the present invention can be used for other purposes in addition to the antifogging use.

In particular, the method consists of a first step for directly nano-structuring the optical element surface by means of plasma etching, and a second step for coating the nano-structured surface with a transparent hydrophilic film that is stable in water and only a few nanometers thick. The nano-structuring is directly made on the body of the optical element, in absence of films or layers deposited on it, and it does not alter the transparency of the polymer because the average distance and width of the nano-structures do not exceed the wavelength of visible spectrum, i.e. the nano-structures obtained according to the invention have width and distance dimensions between them smaller than 400 nm.

The material of the optical component to be treated is a transparent plastic material suitable for said use, such as for example polycarbonate (PC), polymethylmethacrylate (PMMA) and polyolefins such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polystyrene (PS), polyethylene (PE), polypropylene (PP) or similar.

According to a preferred aspect of the invention, the processing of plasma etching extends into the surface of the component material to a depth from 50 nm to 1000 nm, preferably between 100 nm and 600 nm, more preferably between 200 nm and 400 nm and even more preferably between 300 nm and 400 nm.

According to another aspect of the invention, the plasma etching processing is performed in a low pressure capacitive coupling plasma reactor. The plasma is
fed with oxygen or fluorocarbon gas or mixtures thereof, but preferably only oxygen at a flow rate in the range from 5 to 100 seem (standard cubic centimeters per minute), the pressure is in the range 30-200 mTorr, and preferably between 50 and 100 mTorr with a power approximately in the range 0.1 -1 W/cm³, for a time within the range 5-20 min.

This process allows a proper nanostructuring on plastics to be obtained even without pre-deposition of an initial layer, contrary to previous patents that disclose this step.

According to an advantageous aspect of the invention, the second method step, which is the deposition of a hydrophilic film on the surface provided with the aforementioned nano-structures, is performed in the same reactor in which the first step of plasma etching or nano-structuring of the optical element body is carried out.

In a preferred aspect of the invention, the hydrophilic film has a thickness in the range of 10 nm and 50 nm.

This film is preferably inorganic, e.g. composed of silicon oxide, SiOₓ with stoichiometric ratio x between 1.5 and 2.0, preferably within 1.7 and 2.0 and most preferably as close as possible to 2. The material of the film can be defined by its contact angle with water (WCA) and is such that when the material is deposited as a film on a smooth flat surface (e.g. glass or crystalline silicon) its contact angle with water is less than 50°, preferably equal to or less than 35° and more preferably less than or equal to 15°.

In the preferred embodiment of the invention, the film that is deposited on the nanostructure with the above mentioned thickness is composed of silica oxide SiOₓ having stoichiometric x ratio within the range of 1.7 to 2.0, where the content of Carbon is originated substantially only from surface contamination and not from C-Si bonding; i.e. the C is present on the surface in the absence of C-Si bonds (no C-Si bonds are present). The presence or absence of C-Si bonds can be detected with an XPS (X-ray photoelectron spectroscopy) analysis, with monochromatic source, by examining the photoelectronic peaks relevant to silica. These peaks should confirm the presence only of bonds Si(-
0.3, e.g. a signal Si2p symmetrical that falls at 103.5 eV (+/-0.2) having a width at half of its height that is 1.8-2.2 eV.

Other materials suitable to form an anti-fogging film are materials that are inert in water and that can be deposited as thin films conforming to the nanostructured surface. For these materials too, the relevant Water Contact Angle on a film of said material deposited on a smooth surface is less than 50°, preferably less than 35° and most preferably less than 15°.

Indeed, it was found that if the hydrophilic film as defined above presents (on a smooth surface) a contact angle below 50° a significant anti-fog effect is obtained and that this effect is stable over time, until at least 12 months, if the contact angle is equal to or less than 35°. A contact angle less than 15° allows for long life of the desired properties even when the height of the nanostructures is relatively low, for example, between 80 and 200 nm.

According to a particular aspect of the invention, the deposition of SiOx thin film with x ≈ 2 is carried out in a low pressure plasma reactor with capacitive coupling, feeding the plasma with generic organosilanes precursor, but preferably hexamethyldisiloxane (HMDSO) in mixtures with oxygen or mixed with oxygen and argon. The ratio of oxygen to organosilane is in the range between 25 and 50 (seem / seem) at a total flow rate between 100 and 200 seem, pressure between 70 and 200 mTorr and power density in the range of 0.4 and 1 W/cm³. The time length of the process in the reactor is chosen in order to obtain a thickness in the range 10-50 nm, and usually ranges from 20 s to few min (e.g. 6-8 min).

Preferred embodiments are those in which the above discussed contact angle (WCA) is equal to or less than 35° with a height of nanostructures at least of 200 nm and width and distance below 400 nm. Also preferred embodiments are those wherein the said contact angle (WCA) is equal to or less than 15° with a height of nanostructures at least of 100 nm, width and distance below 400 nm.

Finally, preferential embodiments are those with the above defined contact angle of the film that is equal to or less than 15°, height of nano-structures that is at least 300 nm and width and distance that is less than 400 nm.
The invention has several advantages over the prior art. Through the combined plasmochemical process object of this invention, it is possible to provide the surfaces of transparent plastics with very hydrophilic ("superhydrophilic") and stable character, or properties. The performance has been tested in detail on polycarbonate, polymethylmethacrylate, polystyrene and other transparent polymers.

Another important advantage of this invention is that the highly hydrophilic thin film characteristics (contact angle on smooth flat surface that is less than 35 °, but preferably less than 15 °) and the presence of the previously described nano-structures mean that the water-solid contact on these surfaces comes in a permeation regime, i.e. that a thin liquid film is formed, extending over the surface (see fig. 3). This liquid film results in a maximum anti-fog effect (light transmission is not reduced at all) and because of the extended surface, the extended liquid film quickly evaporates. The surface treated according to the invention has an angle ACA measured according to standard ASTM D7334-08, that is equal or less than 30°, preferably less than 10° and most preferably within the range of 0° to 6°; this surface has an exceptional antifogging behaviour.

Moreover, the anti-fog behavior of these surfaces, combining nanometric structure (physical characteristic) and hydrophilic character (chemical characteristic), is stable over time; it was experimentally verified that the treated material according to the invention maintains the same performance for more than four months and surely for at least 12 months.

Because of the inorganic nature of the thin film deposited on nanostructures, the film provides a mechanical strength greater than or equal to that of the pristine polymer/optical element. Moreover, the nano-structuring process by plasma etching allows to reduce reflection of light on the surface, and thus increase the transmission (moth-eye effect). This effect occurs when (i) nano-structures have width and average distance such that, as reported above, scattering is avoided and transparency is ensured (i.e., having size and distance between them less than the
wavelength of visible light, 400 nm) and (ii) a height exceeding 100 nm but preferably above 200 nm.

**Brief description of the figures.**

The invention will now be described in greater detail with reference to the drawings attached as illustrative and not limiting, in which:

- Figs. 1-4 is a diagram that illustrates the different wetting and visibility of a treated surface (Fig. 3 and 4) with respect to the same untreated surface (Fig. 1 and 2);
- Fig. 5 is a diagram showing a manufacturing process of a surface in accordance with the present invention;
- Fig. 6 is a diagram of reactor suitable to carry out the process of the present invention;
- Fig. 7 and 8 are photographs showing the different behavior of the same material without and with surface treatment according to the invention, and
- Fig. 9 is a graph showing the behavior in time of a surface treated according to this invention with respect to known surfaces.

Referring initially to Figs. 1 and 2, it is shown warm moist air condensing on a transparent cold surface 1, that was not treated according to the invention; condensation causes fogging by depositing on the surface a set of micro-drops 2 with round shape that causes internal reflections of the light transmitted through the polymer material (see Figure 2).

Fig. 3 and 4 show the different arrangement of condensed water on a surface 3 treated with the method according to the invention: in this case instead of a drop a liquid film 4 is formed, that does not alter the light transmission (Fig. 4).

With reference to Fig. 5, the process according to the invention provides to initially submit (step A in Fig. 5) at least one surface 5 of a transparent plastic material 6 to a plasma etching treatment to obtain a nanostructured surface 5. The plastic is of the type suitable for use in a component or in an optical element such as, for example, polycarbonate (PC), polymethyl methacrylate (PMMA) and polyolefins such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polystyrene (PS) Polyethylene (PE),
polypropylene (PP) or similar.
The plasma etching processing is carried out in a way known in the art, for example as described in "R. Di Mundo, F. Palumbo, R. d'Agostino, Nanostructuring of polystyrene in fluorocarbon plasmas: from sticky to slippery superhydrophobicity, Langmuir, 24, 5044-5051, (2008) possibly modified as per the following details.

More specifically, with reference to Fig. 6, the treatment involves the following operative parameters. The treatment by plasma etching is carried out in a stainless steel plasma reactor 7, at low pressure and with capacitive coupling; the reactor is provided in a known manner with an upper electrode 14 and a lower electrode 15 and vacuum means such as rotary pump 8 and turbo molecular pump 9. There can be one pump, only. The electrode 14 is connected to the ground and electrode 15 is powered with RF.

The pressure in the reactor is controlled with a pressure transducer 10 and the plasma is fed with oxygen or fluorocarbon gas or mixtures thereof coming from the corresponding sources of gas through flow rate regulators 11 and 12; preferably, only oxygen is fed to the reactor.

In the embodiment shown in Fig. 6, the gas, or the gas mixture, is fed to a ring nozzle 13 positioned near top electrode 14. The flow rate is preferably within the range of 5 to 100 seem (standard cubic centimeters per minute), at a pressure within the range 30-200 mTorr, preferably in the range 50-100 mTorr, with a power density within the range 0.1 - 1 W/cm³, for a time within the range 5-20 min.

The cm³ used to define the power density refer to the volume between the two electrodes, 13 e 14, in the reactor, as the power supplied is divided by the volume of the space between the two electrodes.

This process allows to provide a proper nano-structure on plastic materials directly on the surface of the body, even without the step of pre-depositing an initial layer, which step is required by previous techniques.

The plasma etching processing leads to a roughening of the surface due to its nanostructuring, i.e. a physical change at nanometers level of surface 5, on
which depressions are created and the treatment is controlled to obtain a
modification of the surface through a series of nano-structures in the form of
depressions 7 (separated by corresponding reliefs) that extend into the surface
of the material to a depth of at least 50 nm and typically in the range between
50 nm and 1000 nm. Such depth, which corresponds to the height of the
depressions, i.e. of the nano structures 7, is preferably between 100 nm and
600 nm, more preferably between 200 and 400 nm and even more preferably
between 300 and 400 nm. When the height of the depressions is at least above
100 nm an additional anti-glare effect of treated surface is obtained.

As mentioned above, the average width L and the average distance D between
the nano-structures (or depressions) 7 is less than 400 nm and preferably is in
the range between 50 nm and 400 nm.

The following step, indicated as B in Fig. 5, provides to deposit a thin layer, or
film, 15 of a hydrophilic material on the nano-structured surface 5; this step,
too, is done with a plasma process. The thickness of the deposited film 15 is
preferably within the range of 10 nm to 50 nm.

Materials suitable for the deposition on the nano-structures 7 are preferably
inorganic and they are anyway those who are able to provide, when deposited
with the same method and with the same thickness on a flat, smooth surface
(e.g. glass or crystalline silicon) a thin layer or film that has such a contact
angle (WCA, water contact angle measured as ACA - advancing contact
angle) with a drop of water that is less than 50°, preferably less than or equal to
35° and more preferably less than or equal to 15 degrees.

The contact angle is measured as "advancing" (ACA) contact angle in
accordance with ASTM D7334-08, i.e. by using drops of distilled water with a
volume between 1 and 20 µL, preferably between 1 µL and 5 µL, and measuring
the angle as soon as the droplet comes in contact with the surface. Further
details on the procedure for the evaluation of the contact angle are shown in
the experimental part of the aforementioned paper by Mundo et al., Langmuir,

The hydrophilic film is preferably inorganic. A preferred film is composed of
silicon oxide, \( \text{SiO}_x \) with stoichiometric ratio \( x \) between 1.5 and 2.0, preferably 1.7 to 2; other materials that can also be suitable are those inert in water, that can be deposited in the form of thin films following the nano-structured surface. As mentioned above, the coatings that can be used are those which, when deposited under the same conditions (i.e. with the same method of the invention) on a flat, smooth surface such as glass or crystalline silicon, are able to provide a contact angle with distilled water (measured in accordance with the above mentioned standard) that is lower than 50 °, preferably less than or equal to 35 ° and more preferably less than or equal to 15 °.

According to a particular aspect of the invention, the deposition of \( \text{SiO}_x \) thin films with \( x \) within the range 1.7-2.0 and preferably about 2.0, is done in the low pressure plasma reactor, with capacitive coupling, shown in fig. 6, provided for this purpose with a source of organosilanes (HMDSO) and a source of argon (Ar). The present invention makes it possible, if desired, using the same reactor to perform in succession the two steps of the claimed method.

A film as defined above is substantially free of carbon \( \text{CH}_x \) groups arising from the organosilane used in plasma deposition process.

A film as above defined is substantially free from carbon groups \( \text{CH}_x \) deriving from the organosilanic compound used in the deposition plasma process. In particular \( \text{SiO}_x \) films are preferred where the superficial (surface) content of Carbon as detectable with an XPS (X-ray photoelectron spectroscopy) analysis, with monochromatic source, is only deriving from surface contamination. This corresponds to photoelectronic peaks relevant to silica that show the presence only of bonds \( \text{Si}(-\text{O})3\text{-}4 \) (e.g. a signal \( \text{Si}2p \) symmetrical that falls at 103.5 eV (± 0.2) having a width at half of its height that is 1.8-2.2 eV). Such a film of silica oxide is able to provide the best performances.

The plasma is in fact supplied by an organosilane precursor, preferably hexamethyldisiloxane (HMDSO) in mixtures with oxygen or mixed with oxygen and argon, with a ratio of oxygen to organosilane in the range between 25 and 50 (seem / seem) at a rate of total flow between 100 and 200 seem; at a pressure between 70 and 200 mTorr and with a power density in the range of
0.4 and 1 W/cm³.
The treatment time is generally comprised within the range of 20 s - 6 min, and however for a time enabling to obtain a deposited film thickness in the range 10-50 nm.

As discussed above, the deposited film follows the shape of the nanostructures and gives to the surface a superhydrophilic character, this means that the water deposited on the surface extends over the entire surface forming a substantially uniform thin layer, or, in other words, that the surface has a contact angle with water that is within zero and 6 degrees and preferably is 0°.

It is important to note that the second treatment of the optical element surface surprisingly allows to obtain a surface with superhydrophilic behavior starting from a surface that initially undergoes a treatment, plasma etching, which is normally used to impart hydrophobic properties to such surface.

The invention will now be described in more detail with reference to the following not exhaustive examples.

Ex 1 - preparation of a nanostructured surface

A Polycarbonate slab with dimensions 1.5 cm x 1.5 cm was treated with plasma etching under the following conditions: oxygen flow rate of 10 seem, chamber pressure of 100 mTorr, power density of 0.36 W/cm³ for a time of 10 min. The resulting nanostructures on the surface have an average size of 400 nm in height with a width of 100 nm and a distance of 300 nm, as measured with a scanning electron microscope.

Ex 2 - coating of the nanostructured surface with a film

In the same reactor of ex. 1, without opening the chamber, a film deposition was subsequently earned out by feeding the plasma with hexamethyldisiloxane (1.5 seem), oxygen (100 seem) and argon (50 seem) at a pressure of 100 mTorr and a power density of 0.4 W/cm³, for a time of 1 min; a thickness of 30 nm was obtained. Through examination with a scanning electron microscope it was found that this coating is reasonably conform to the nanostructured surface.

The contact angle with distilled water of this film, applied under the same conditions on flat and smooth glass surface was measured as "advancing
contact angle" (ACA) in accordance with ASTM D7334-08 and found to be 5°. The same measurement carried out on samples of optical elements obtained by Example 2 was found to be zero.

**Ex 3 - comparative tests between surfaces**

The fogging test was conducted on samples obtained from example 2, the modified sides of the samples were maintained for a time of 3 min on a cylindrical flask with a volume of 2 ml half filled with water and brought to a temperature of 70 °C. The samples were then observed with white light in transmission with a video camera at low magnification, to determine both the darkening and its duration. While on the untreated samples there was a darkening (blinding) and very persistent fog (depending on the material from 30 s to 2 min) on those modified according to the above described conditions, the formation of a clear liquid was observed which evaporated in few seconds (2 - 8 s). This behavior was also observed after 4 months from the surface treatment on specimens preserved in non-sealed boxes, as well as on specimens tested for several repetitions.

Figures 7 and 8 shows the images of the specimens just removed from steam: fig. 7 refers to the sample of untreated PC and fig. 8 to PC treated in the conditions of Example 1 and 2.

As it can be seen, the untreated PC in Fig. 7 is "opaque" whilst the treated material in Fig. 8 is transparent. The untreated material in Fig. 7 looses fogging in one minute while for the modified (Fig. 8) sample the film of water, transparent, disappeared by evaporation in 5 seconds.

**Ex 4 - comparative tests on the stability of the superhydrophilic properties.**

Five samples were prepared according to the procedure of example 2, i.e. they were provided with a nanostructured surface having nanostructures with height of at least 200 nm and with width and distance both being less than 400 nm; the nanostructures were coated with a SiO₂ film having a thickness of about 30 nm. As comparison tests the following samples were prepared:

- n. 5 samples of the same substrate material (polycarbonate) were
treated according to example 1 to provide them only with nanostructures;
- n. 5 samples of the same base material (polycarbonate) treated to provide them only with a SiO\textsubscript{x} film according to example 2.

An evaluation of the antifogging properties of the final materials was obtained directly with the technique of measuring the contact angle; the contact angle was measured, as above discussed, as the advancing contact angle (ACA) according to standard procedure ASTM D7334-08; the lower is the angle value, the better are the antifogging properties. More in particular, on the samples the visual measurement of example 3 was carried out, and also the ACA angle on the treated surface was measured. From the data obtained, surfaces having an ACA angle of less than 30° (30 degrees) are antifogging, surfaces with ACA angle of less than 10° are preferred. Surfaces according to the preferred embodiment of the invention have an ACA within the range of 0 degrees to 6 degrees.

The stability of the surfaces having only nanostructures, surfaces having only SiO\textsubscript{x} film and surfaces having both nanostructures and SiO\textsubscript{x} film (i.e. the surfaces according to the present invention) is expressed as ACA values in the graph of figure 9.

The measures were carried out on the day of treatment of the surfaces, after 1 month from treatment and after 12 months from treatment; samples were exposed to ambient atmosphere under identical conditions. The graph of fig. 9 shows the importance of the combination of nanostructures and SiO\textsubscript{x} film in order to reach a stable superhydrophobic effect. In fact the highly hydrophilic affect initially present both on the nanostructured polymer and on the SiO\textsubscript{x} film (only) is lost in about one month when the element is exposed to ambient air.

**Ex 5 - stability to water**

Five samples obtained according to the procedure of example 2 were immersed in bidistilled water (ca 100 ml) for 24 hours. The samples were then extracted from water and dried initially by blowing nitrogen and subsequently by leaving at ambient air for 2 hours. Measures of their ACA angle and of their
anti-fogging properties were carried out as above. The measures gave identical results on the same sample after 7 repetitions of the immersion test, i.e. the ACA values were in the range of 0 to 6 degrees, no fogging appeared, the condensed water formed a thin film that evaporated in few seconds (2 to 8 seconds).

Similar conditions, but with slight variations in processing times have been used to treat samples of other polymers (PS, PMMA, etc.) to obtain the same structure. The results were satisfactory as well.

It is important to specify that the procedure object of this invention, depending on the application, can be performed on one surface 5, or on both surfaces, 5 and 8, of the transparent polymer 6. In addition, it can be combined in order to have on a surface the modification described above and on the other surface a modification aimed to other performances, but anyway based on a plasmochemical nanostructuring process.

The following possibilities may therefore be provided:

1) side 5: superhydrophilic / side 8: unmodified

2) side 5: superhydrophilic / side 8: superhydrophilic

3) side 5: superhydrophilic / side 8: superhidrophobic (water repellent)

In case 3), side 8 of the element is submitted to a process of nanostructuring via plasma etching and to a subsequent deposition of a chemically hydrophobic thin film (SiC$_x$H$_y$, CF$_z$)

4) side 5: superhydrophilic / side 8: anti-reflective

Thanks to this latter combination and in view of the fact that reduction of the reflection is more efficient if it occurs on both sides of the transparent material, it is possible to foresee configurations described in 1), 2) and 3) with the process on the side 5 optimized to operate at the same time as superhydrophilic and anti-reflecting.
CLAIMS

1. An optical element, which includes a body (6) made of transparent plastic material, said body having a first (5) and a second (5') surface, characterized in that at least one of the said surfaces (5, 5') is provided with a plurality of nanostructures (7) obtained directly on said at least one of the said surfaces (5, 5') of the said body (6), said nanostructures having mean width (L) and mean distance (D) of less than 400 nm, and in that said surface provided with said nanostructures is covered at least in part by a film (15) of hydrophilic material and has hydrophilic and antifogging properties.

2. An optical element according to claim 1, wherein said nanostructures (7) extend from the surface to a mean depth between 50 and 600 nm, preferably between 200 and 400 nm.

3. An optical element according to any previous claim, wherein the thickness of said film (15) is within the range 10-50 nm.

4. An optical element according to any previous claim, wherein said film (15) is made of a material such that the contact angle with a water drop (WCA) of said film coated onto a flat surface, measured as advancing contact angle according to the ASTM D7334-08, is 35° or less and preferably 15° or less.

5. An optical element according to any previous claim, wherein said film (15) is made of silicon oxide, SiO\(_x\) with stoichiometric ratio \(x\) within the range of 1.5 to 2.0, preferably 1.7 to 2.0.

6. An optical element according to claim 5, wherein said SiO\(_x\) film has a content of superficial Carbon, as detectable with an XPS (X-ray photoelectron spectroscopy) analysis, with monochromatic source, is only deriving from surface contamination, and wherein C-Si bonds are not present on said film.

7. An optical element according to any previous claim, wherein said treated surface has an ACA angle measured according to the ASTM D7334-08,
that is 30° or less, preferably less than 10° and more preferably within the range of 0° to 6°.

8. An optical element according to claim 6 or claim 7, wherein said second surface (5') is provided with a nanostructure and with a film that is selected between hydrophobic and hydrophilic materials.

9. A method for producing and imparting hydrophilic and antifogging properties to an optical element according to any of the previous claims, characterized by comprising the following steps:
   a) obtaining a plurality of nanostructures (7) via a plasma etching treatment, directly and without a film pre-deposition, onto at least one of the surfaces (5, 5') of the body (6) of said element;
   b) coating at least part of said surface bearing nanostructures with a film (15) of hydrophilic material by deposition in the reactor in which step a) was carried out.

10. A method according to claim 9, wherein the deposition step of the hydrophilic film (15) is carried out with a material such that the contact angle (WCA) of said material applied onto a flat surface, measured as advancing contact angle according to the ASTM D7334-08, is equal to or less than 35° and preferably 15° or less.

11. A method according to the claim 9 or 10, wherein said film (15) is deposited by feeding an organosilane precursor, mixed with oxygen or mixed with oxygen and argon, the ratio of oxygen to organosilane being in the range between 25 and 50 (sccm/sccm) at a total flow rate between 100 and 200 sccm, pressure between 70 and 200 mTorr and power density in the range of 0.4 and 1 W/cm³.

12. A method according to claim 11, wherein the obtained film (15) is made of silicon oxide, SiOₓ with stoichiometric ratio x within the range of 1.5 to 2.0, preferably 1.7 to 2.0 and most preferably of about 2.0.

13. An element as obtainable by the method according to any claim 9 to 12, characterized in that the surface provided with an hydrophilic film on nano-structures is provided with an ACA angle value, as measured
according to ASTM D7334-08, that is 30° or less, preferably less than 10° and more preferably within the range of 0° to 6°, said value being stable for a period of time of at least 12 months.
Fig. 5
Fig. 9
## A. CLASSIFICATION OF SUBJECT MATTER

INV. G02B1/10  G02B1/11  C23C16/40

### ADD.

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

## B. FIELDS SEARCHED

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

- G02B
- 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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

- Further documents are listed in the continuation of Box C.
- 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

**Date of the actual completion of the international search**

3 November 2011

**Date of mailing of the international search report**

25/11/2011

**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, 340-3016
- Fax: (+31-70) 340-3016

Stemmer, Michael
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>US 2010033819 Al</td>
<td>11-02-2010</td>
<td>WO 2008104150 Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 102007009512 Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2118691 Al</td>
</tr>
<tr>
<td>US 2009169822 Al</td>
<td>02-07-2009</td>
<td>JP 2009175729 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TW 466632 B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2009127581 Al</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2011051246 Al</td>
</tr>
</tbody>
</table>

Form PCT/ISA/210 (patent family annex) (April 2005)