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<p>(54) Title: <b>HARDCOATS FOR FLAT PANEL DISPLAY SUBSTRATES</b></p> <p>(57) Abstract</p> <p>The present invention relates to a unique hard coating that provides the necessary characteristics for flat panel display plastic substrates because the coating is amorphous and is comprised of C, H, Si and O. The coating of the present invention is hard, optically transparent, scratch and abrasion resistant and hydrophobic. It is deposited by a low density, low temperature plasma enhanced chemical vapor deposition (PECVD) process and exhibits excellent barrier protection and reduced permeability to moisture, oxygen, helium and other vapors.</p>		

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1 **Hardcoats for Flat Panel Display Substrates**

2 **Field of the Invention**

3 The present invention relates generally to transparent hard coatings on plastic  
4 substrates for flat panel displays. More particularly, the present invention relates to a  
5 coating comprised of carbon, hydrogen, silicon and oxygen.

6 **Background of the Invention**

7 Flat Panel Displays (FPDs) have a wide range of consumer, industrial and military  
8 applications and are projected to exceed \$20 billion dollars by the year 2000. Of the many  
9 types of FPD technologies, Liquid Crystal Display (LCD) technology leads the pack and is  
10 most mature. The profit margins in the LCD market are becoming increasingly low,  
11 because of the changing market. There is an increased push to reduce the material cost in  
12 making FPDs which is estimated to be about 40 to 50% of the total display cost. There is a  
13 thrust towards looking at new materials, decreasing weight, reducing display thickness,  
14 improving viewing angles and lowering back illumination.

15 One of the key challenges to making the next generation, low weight FPDs is  
16 replacement of glass displays with plastic displays. Plastic displays are lower weight,  
17 shatter resistant and can provide equivalent transmission properties to that of glass.  
18 However, plastics such as polycarbonates and polyethylene terephthalates (PET) are not  
19 scratch and abrasion resistant. It is important to provide a hard coating to the plastic with  
20 good transmission and refractive index matching to effectively function as flat panel  
21 displays. Another disadvantage of plastics is they are permeable to liquids and vapors,  
22 which is undesirable. Permeation of water vapor, oxygen, liquid crystals and other gases  
23 could ruin the electronics behind the flat panel display, if proper barrier protection is not  
24 provided. Thus the hard coating also needs to be impermeable to liquids, vapors and  
25 solvents used in the FPD manufacturing.

1           The markets for plastic substrate FPDs is quite huge, prominent being the LCD  
2 market. Plastic substrate displays could be used in LCD applications, which currently use  
3 soda-lime glass displays. This is a sizable portion of the display market and can be as high  
4 as 5 billion square inches by year 2000. The LCD applications, where hardcoated plastic  
5 displays could be used, include consumer applications such as clocks, watches, calculators,  
6 games, personal digital assistants (PDAs), phones, televisions, camcorders, cameras and  
7 industrial applications include PCs, medical instruments, facsimiles, thermostat meters,  
8 industrial displays, test equipment etc.

9           There are a number of hardcoats that are available in the industry. The predominant  
10 coatings which might be considered as hardcoats are DLC and polysiloxane dip coatings.  
11 Conventional DLC coatings consist of carbon and hydrogen with no silicon and oxygen.  
12 Polysiloxane coatings are deposited by spin coating, spraying or dipping followed by a  
13 curing step or UV hardening.

14           Dip coatings, are wet chemical processes which require significant handling and  
15 several hours to go through the coating process. Also, the chemicals used are partially  
16 toxic and combustible, making them increasingly difficult to handle due to environmental  
17 considerations. The present invention has the potential of depositing coatings at high  
18 deposition rates, which is cost-effective, requires minimum handling and is benign to the  
19 environment.

20           The present invention is a low temperature process capable of depositing on heat  
21 sensitive plastics such as polycarbonates and polyethylene terephthalates. The substrate  
22 temperature does not exceed 70°C during normal operation. However, active cooling of  
23 the substrate temperature is possible and the substrate temperature can be maintained at  
24 room temperature. Because the present invention involves a low temperature process,  
25 there is no thermal mismatch issue between the substrate and the hard coating. DLC  
26 processes typically require higher temperatures (as high as 200°C) and hence adapting the

1 DLC technology to coating low temperature materials is a significant problem. The present  
2 invention can be deposited on substrate materials as thin as 0.075 mm while some dip  
3 coating polysiloxane processes require rigid substrates (minimum thickness ~ 1 mm).

4 DLC coatings exhibit high compressive stresses (sometimes 5 times that of the  
5 present invention) resulting in poor adhesion to substrates. The poor adhesion of DLC  
6 necessitates the use of interlayers to improve adhesion, which is not required in the present  
7 invention.

8 The present invention yields an extremely hard coating compared to polysiloxane  
9 dip coatings. The polysiloxane hard coatings are not as abrasion resistant as glass. DLC  
10 coatings are harder than the present invention, but because of their increased hardness they  
11 exhibit high internal stress and hence require interlayers to promote adhesion.

12 Petrmichl et al (U.S Patent No. 5,618,619) discusses an abrasion resistant coating  
13 deposited using an ion-assisted process with nanoindentation hardness of 2 to about 5  
14 GPa. The coatings of Petrmichl et al are softer than the present invention and their  
15 effectiveness as a barrier coating is unknown. Also the invention of Petrmichl et al teaches  
16 the use of only siloxane or silazane with oxygen. This limits the highest coating hardness  
17 that can be achieved. The use of hydrogen in addition to oxygen and siloxane or silazane  
18 precursors is novel in the present invention and allows achieving higher hardnesses.

19 Petrmichl et al does not indicate the nature of bonding between the C, H, Si and O in the  
20 material. It is well known to one skilled in the art of materials science and engineering that  
21 the bonding between these coatings influences the properties of the material.

22 Lin et al<sup>1</sup>. have reported on depositing SiO<sub>2</sub>-like films using siloxane and oxygen as  
23 precursor materials by high-density microwave electron cyclotron resonance discharge.  
24 The resulting coating material is different from the present invention and consists mainly of

1 a silicon dioxide. Fourier Transform Infrared Spectroscopy (FTIR) indicates presence of a  
2 SiO<sub>2</sub>-like band (towards higher wavenumbers and sharper Si-O stretching) and small  
3 amount of Si-CH<sub>3</sub> bonding. The high-density plasma approach utilized by Lin et al is  
4 probably responsible for the different type of bonding, different material density (presence  
5 of micropores) and higher concentration of oxygen observed in the films. Even though Lin  
6 et al have not reported the barrier properties, a microporous coating is expected to have  
7 poor barrier properties. The hardness range of this material is unknown.

8 Dorfinan et al (U.S Patent Nos. 5,466,431 and 5,352,493) describe a diamond-like  
9 coating consisting of C, H, Si and O. The optical transparency of the coatings of Dorfinan  
10 et al. in the UV-visible range is limited and is highly dependent on coating thickness. Thus,  
11 the coatings of Dorfinan et al do not have the same degree of transparency as the coatings  
12 of the present invention.

13 Thus, there is a need in the industry for a coating for plastic substrates, and more  
14 particularly for flat panel displays which can be deposited on the plastic substrate by a low  
15 temperature process at a high deposition rate; and which is cost effective and benign to the  
16 environment; and which produces a coated product that is hard, optically transparent,  
17 impermeable, scratch and abrasion resistant and that have good adhesion.

#### 18 Summary of the Invention

19 The present invention pertains to a unique hard coating that can provide the  
20 necessary characteristics for flat panel plastic substrates. The coating is amorphous and is  
21 comprised of C, H, Si and O. The coating of the present invention is hard, optically  
22 transparent, scratch and abrasion resistant and is deposited by a low density, low  
23 temperature plasma enhanced chemical vapor deposition (PECVD) process. The coating  
24 of the present invention is deposited at low temperatures (below 70°C) and has been  
25 successfully deposited on clear plastics such as polycarbonates, polyethylene terephthalates  
26 (PET), polyethylene, fluoropolymers and olefins.

1           In addition to the above advantages, the coating of the present invention exhibits  
2 excellent barrier protection. The coating can be pore-free and exhibit reduced permeability  
3 to moisture, oxygen, helium and other vapors. The coating is hydrophobic (repels water  
4 and prevents wetting) which results in improved barrier protection.

5           It is a present object of this invention to provide a coating for plastic substrates  
6 that has properties which can be tailored.

7           It is another object of the present invention to provide a coating for plastic  
8 substrates that can be deposited below 70°C, thereby making it possible to compatibly coat  
9 a variety of flexible substrate materials.

10           It is a further object of the present invention to provide a coating for plastic  
11 substrates which has excellent adhesion, high hardness, excellent transparency in the visible  
12 and infrared wavelengths, low film stress, very high resistivity, high degree of flexibility,  
13 UV resistance, good chemical resistance, high degree of environmental stability, low  
14 surface energy and high water contact angle.

15           It is yet another object of the present invention to provide a coating for plastic  
16 substrates that is impermeable to moisture and corrosive gases, thereby providing a  
17 protective barrier for internal circuitry.

#### 18 **Brief Description of the Drawings**

19           Figure 1 is a schematic of a hardcoating deposition chamber.

20           Figure 2 is a comparison of hardness of the coating with uncoated polycarbonate,  
21 bare glass and polysiloxane dip coated polycarbonate.

22           Figure 3 is a typical UV-Vis transmission and reflectance spectra for a coating on  
23 glass.

24

1 **Detailed Description of the Invention**

2           The present invention pertains to using a transparent, hard, wear-resistant carbon,  
3 hydrogen-containing coating on transparent plastic substrates for flat panel displays.  
4 However, one particularly preferred embodiment of the coating of the present invention  
5 comprises carbon, hydrogen, silicon and oxygen in an amorphous structure. The term  
6 "amorphous" used herein refers to a random structure or arrangement of atoms in a solid  
7 state that results in no long range regular ordering, and no crystallinity or granularity.

8           Therefore, the preferred materials used to coat flexible substrates, as described  
9 herein, may comprise predominantly a glass-like Si-O network; or a multi component  
10 structure comprising Si-O, C-H, Si-H and Si-C. In the latter, Si-O and C-H are  
11 predominant with other components being the minority.

12           The carbon content in the preferred diamond-like coatings of the present is greater  
13 than about 25 atomic percent of the coating, preferably from about 25 atomic percent of  
14 the coating to about 65 atomic percent of the coating. Although such coatings may  
15 theoretically be prepared without any hydrogen, the hydrogen content is preferably at least  
16 about 1 atomic percent of the coating up to about 40 atomic percent of the coating. The  
17 silicon content ranges from about 10 atomic percent of the coating to about 30 atomic  
18 percent of the coating, while the oxygen content ranges from about 8 atomic percent of the  
19 coating to about 40 atomic percent of the coating. The density of the coating varies from  
20 about 1.7 gm/cc to about 2.0 gm/cc.

21           The preferred coatings of the present invention are hard carbon, silicon-containing  
22 coatings synthesized via a RF discharge plasma process which as a general process would  
23 be readily understood by one skilled in the field of thin film deposition. Carbon and silicon  
24 -containing radicals can be produced by a plasma discharge and deposited on a substrate  
25 applied with a high-voltage field in a vacuum chamber.

1           Figure 1 shows one preferred embodiment of the coating chamber used for  
2   depositing the preferred hard coatings. A vacuum deposition chamber 100 is provided to  
3   coat a substrate sample. A precursor inlet system 110, comprises a metal tube and a gas  
4   distribution ring through which a liquid precursor, preferably a low vapor pressure  
5   siloxane, is injected. The precursor inlet system 110 is shown incorporated into the  
6   chamber 100 through the sidewall of the chamber. An alternate arrangement is  
7   introduction of the precursor into the chamber 100 through the top of the chamber 115 via  
8   a gas showerhead. The samples are loaded into the chamber from the top of the chamber  
9   115 or through a load lock (not shown). The chamber comprises a cylindrical enclosure  
10   with top and bottom parallel 117. A power supply is used for biasing the electrodes (RF-  
11   13.56 MHz). In practice, the system is "pumped down" using conventional vacuum  
12   pumpdown procedures. Gate valves and foreline valves (not shown) are closed and the  
13   system is backfilled with dry nitrogen or argon until the chamber reaches atmospheric  
14   pressure. The top of the chamber is then opened and substrates 150 to be coated are  
15   placed on the electrodes using any fixtures or fastening means including clips, screws,  
16   clamps, tape etc.

17           The precursor is introduced into the deposition chamber by liquid-to-vapor  
18   delivery system. The liquid-to-vapor delivery system is a conventional off-the-shelf  
19   component known in the field of vacuum technology. The precursor is stored in a reservoir  
20   and is delivered to a flash evaporator, if required. The precursor is flash evaporated into a  
21   vapor. A mass flow controller is used to precisely control the flow rate of the precursor  
22   liquid through capillary tubing. While not required, a mixing gas, such as argon can be  
23   used to assist precursor evaporation.

24           The high vacuum is achieved by roughing down the chamber with a mechanical  
25   pump followed by pumping with a roots blower pump. Other pumping systems, with or  
26   without traps, such as turbomolecular pump, cryogenic pump, or other high vacuum

1 pumps known in the field of vacuum technology can also be used. The coatings required  
2 according to the process of the present invention can be carried out in a batch type process  
3 for small volumes. In such instance, the substrates are mounted on a substrate holder  
4 inside the deposition chamber, the chamber is evacuated, the deposition is performed, and  
5 the chamber is vented, followed by removal of the coated parts (substrates).

6 For larger volumes, the process of the present invention can be carried out in a  
7 roll-to-roll system. Such a roll-to-roll system could consist of cleaning module, transport  
8 mechanism to wind and unwind rolls, and mechanized/robotic loading of the parts into the  
9 system. It is understood that the substrates to be coated may be rotated, tilted, or  
10 otherwise oriented, or manipulated while on the substrate holder, and at other instances  
11 during processing.

12 Vertical orientation of the substrate is preferred to minimize particulate or debris  
13 accumulation and contamination of substrate surfaces. The deposition chambers are  
14 evacuated with low turbulence vacuum pumping to minimize particulate and debris being  
15 deposited on the substrate surfaces.

16 The chamber is evacuated to a base pressure below 10 to 20 mTorr after loading  
17 the substrates. During deposition the chamber pressure is in the range of 50 to 500 mTorr.  
18 The chamber pressure is increased by introduction of the precursor and additional gases  
19 such as argon, hydrogen and/or oxygen. A throttling valve could also be used to adjust the  
20 chamber pressure. The substrates are ion cleaned inside the deposition chamber before  
21 coating.

22 Substrate plasma cleaning can be performed with a number of gases, such as argon,  
23 oxygen and hydrogen. The choice of the gas during plasma cleaning depends on the type  
24 of substrate. Substrate plasma cleaning is performed by RF glow discharge. Cleaning gas is  
25 introduced until the chamber pressure is in the 50 to 500 mTorr range. Powering the  
26 electrode(s) with a RF potential excites a glow discharge. During the discharge, a

1 substrate bias of from about 0.005 to about 5.0kV can be used. The frequency of the RF  
2 is fixed. However, other frequencies (100 KHz to 100 MHz) can also be used. Other ion  
3 sources known in the field of deposition coating such as, Kaufmann type ion sources, RF  
4 coil, ECR sources etc. can also be used for ion generation. The plasma cleaning process  
5 has been found to efficiently remove hydrocarbon contamination, and other contaminants,  
6 as well as improve the adhesion of coatings deposited on substrates.

7 Towards the end of the substrate cleaning, vaporized organosilicon precursors,  
8 preferably siloxanes which contain C, H, Si, and O are introduced into the chamber. The  
9 precursor can be introduced into the system using liquid-to-vapor delivery systems  
10 consisting of flow controller, a heater, and a dispenser as known in the field. The  
11 precursors preferably have 1 to 10 silicon atoms. The preferred precursor is HMDSO and  
12 is transported to the chamber using a carrier gas such as argon. Along with the precursor,  
13 additional gases such as hydrogen and oxygen are introduced. Other gases such as  
14 methane, acetylene, butane,  $CF_4$ ,  $C_2F_6$  can be used for altering film properties. The RF  
15 plasma discharge causes fragmentation and ionization of the precursor.

16 Variations of the above described deposition process include: (a) the use of  
17 sputtered silicon and oxygen gas as sources for Si and O; (b) use of solid  $SiO_2$  as a source  
18 for Si and O; (c) use of  $SiH_4$  and oxygen-containing gases as sources for Si; (d) use of a  
19 graphite target, hydrogen, and hydrocarbon gases as sources of C and H. Combination of  
20 the aforementioned methods may be used. The coating deposition preferably is sustained  
21 by a RF capacitively coupled discharge (CCD).

22 A single plate configuration can be used. The substrates are attached to the plate.  
23 RF or PDC voltage is then applied. In the case of a capacitive RF discharge, the frequency  
24 of the RF is in the range of 100 kHz to 100Mhz. In another method, a large RF antenna  
25 can be placed inside the chamber to excite the discharge. The antenna can be made of

1 copper, stainless steel, or other known state of the art materials. A protective coating,  
2 such as porcelain, can be applied to the surface of the antenna to prevent sputtering.

3 A RF potential is generally applied to the substrates during the deposition process.  
4 The RF potential assists in densification and hardening of the deposited coating. The range  
5 of RF potential is about 0.005 to 5 KV can be altered to tailor the coating properties. No  
6 external substrate heating is used. There is generation of heat due to ion bombardment and  
7 this causes substrate heating up to 70°C. The substrate holder can be actively cooled using  
8 closed circuit heat exchanger, if desired.

9 The ability to tailor the coating properties and the ability to deposit these coatings  
10 below 70°C, makes it possible to compatibly coat a variety of flexible substrate materials  
11 such as Polycarbonate, PET, PE, Kapton, Mylar, Ultem and Torlon. It is believed that this  
12 "tunability" and lack of thermal mismatch problems contribute to the coatings' excellent  
13 adhesion and low stress.

14 In addition to excellent adhesion, the coatings of the present invention have high  
15 hardness, excellent transparency in the visible and infrared wavelengths, low film stress,  
16 very high resistivity, high degree of flexibility, UV resistance, good chemical resistance,  
17 high degree of environmental stability, low surface energy and high water contact angle.

18 The coatings have high hardness and elastic modulus as measured by  
19 nanoindentation using a Nanoindenter IIs. Because of the high hardness the coating have  
20 good scratch resistance and endurance. The coatings exhibit hardness in the range of 2 to  
21 10 GPa (typical – 5 to 7.5 GPa). For comparison, the hardness of mild steel is about 3 to 4  
22 GPa and that of glass is about 6 to 8 GPa (Figure 2). Thus the typical hard coatings are  
23 harder than mild steel and are as hard as glass. The typical elastic modulus of hardcoats is  
24 in the range of 30 to 50 GPa. The abrasion resistance of the coating was tested by rubbing  
25 steel wool 6 to 8 times on a coated polycarbonate substrate. The coating passed the steel

1 wool abrasion test successfully. The optical properties of the coating were not  
2 compromised and there was no physical damage to the coating from the steel wool.

3 The coatings have excellent transmission in the visible wavelengths. The coating  
4 transmission exceeds 85% in the wavelength range of 360 to 900 nm. The coating  
5 transmission exceeds 90% in the wavelength range of 400 to 900 nm (Figure 3). The  
6 coating transmission is very high in the infrared range as well. The refractive index of the  
7 coatings can be tailored in the range of 1.6 to 2.5 at 540 nm wavelength.

8 The coatings exhibit very low film stress. The residual stress in the coatings has  
9 been characterized by laser beam deflection technique using the Stoney equation as known  
10 in the state of the art. The residual stress is compressive and is in the range of 90 to 400  
11 MPa. The reason for low stress in the film is credited to the low temperature deposition  
12 process and the unique film structure.

13 The coatings have resistivity exceeding  $10e+13$  to  $10e+14$  ohm-cm at room  
14 temperature. The coatings also have very high dielectric strength and low leakage current  
15 density. The dielectric strength of the coatings is greater than 1 MV/cm and the dielectric  
16 constant is around 3.5 to 5.0.

17 Flexibility of the coatings has been quantified by measuring the lowest radius of  
18 curvature to which coated polyimides (Kapton® and Mylar®) substrates could be bent to  
19 with no cracking or coating delamination. The coatings are resistant to cracking, down to  
20 radius of curvature of  $7/32$ ". The flexibility of the coatings is beyond the requirements of  
21 the flat panel display application. Coatings are more flexible in the convex bending mode  
22 as opposed to the concave bending mode because of the compressive stress in the film.  
23 The resistance to degradation on prolonged exposure to illumination of the coatings has  
24 been investigated. The coatings were subjected to tungsten lamp illumination (equivalent  
25 to 0.5 sun) for about 1500 hours. The coatings showed no change in the optical and  
26 physical properties indicating that the coatings are extremely stable.

1           Good resistance to all of the chemicals associated with FPD fabrication is an  
2 essential property for the plastic hardcoat. The coatings have been tested in accordance  
3 with ASTM D 1308 for resistance to methanol, acetone, IPA, 30% hydrogen peroxide,  
4 and 30% ammonium hydroxide. In all cases, the coating showed no sign of discoloration,  
5 blistering, loss of adhesion, or change in the optical characteristics. The coatings have been  
6 tested for corrosion resistance and chemical inertness in acidic and alkaline environments.  
7 The coatings are not affected by acids such as HCl, HF and HNO<sub>3</sub>, bases such as KOH.

8           In order to withstand the high temperatures required in the fabrication of FPDs, it  
9 is essential that the hard coat, as well as the substrate, be able to withstand 200°C for at  
10 least 1 hour without degradation of its physical or optical properties. Thermal stability  
11 studies performed on these coatings suggest that they can survive temperatures up to  
12 400°C for 2 hours in an oxidizing environment. This is well above the requirements for the  
13 FPD application.

14           Another requirement of hardcoats for plastic displays is barrier protection from  
15 humidity. The coatings have to be impermeable to moisture and corrosive gases so that the  
16 permeation through the underlying plastic substrate is prevented and thus protecting the  
17 internal circuitry of the product. The coatings act as an excellent barrier to oxygen and  
18 water vapor. Coatings have shown reduction in oxygen transmission rate from 1.9 to 80.2  
19 times that of the uncoated polymeric substrates. Coatings have shown reduction in water  
20 vapor transmission rate from 1.4 to 12.1 times that of the uncoated polymeric substrates.  
21 The effective barrier protection is dependent on the choice of the polymeric substrate.

22           One of the key aspects of barrier coatings is their affinity to water. The present  
23 coatings are highly hydrophobic (prevent water from spreading due to low surface energy)  
24 and exhibit a high water contact angle. The higher the contact angle (lower the surface  
25 energy), the lower the wetting of the coated surface by water. The coatings have a surface  
26 energy of 27 to 38 dyn/cm and a water contact angle of 70 to 92.



1 carbon steel substrates were tested. The adhesion was good on all substrates and no  
2 coating delamination or debonding was observed.

3 **Example 3**

4 Cleaned four by four inch square substrates of Polyethylene, Cyclic Polyolefin and  
5 Fluoropolymer were mounted on the bottom electrode. Control samples of silicon, glass,  
6 carbon steel, and stainless steel substrates that were cleaned in a detergent, followed by  
7 Isopropanol and then blow dried with Nitrogen gas were also mounted on the substrate  
8 holder. The chamber was evacuated to an ultimate pressure of 25 mtorr. Argon gas was  
9 introduced in to the chamber to raise the pressure to 180 mtorr. A RF substrate power of  
10 300W was used to bias the substrates for in-situ plasma cleaning. The substrates were  
11 plasma cleaned for 5 minutes. After cleaning the substrate power was ramped up to 538W  
12 which corresponded to a substrate bias of 162 V. Then the precursor was introduced  
13 through the liquid vapor delivery system. The precursor HMDSO was used in this  
14 deposition. A precursor flow rate of 0.06 g/min was used. Additional process gases such  
15 as hydrogen and oxygen were introduced simultaneously. The hydrogen flow rate was 30  
16 sccm and the oxygen flow rate was 45.6 sccm. The deposition was performed under the  
17 above conditions for 38 minutes. The substrate holder temperature after the deposition  
18 was about 50°C. This resulted in a 0.73 micrometer thick, highly adherent coating. The  
19 coating exhibited a hardness of 6.2 GPa on carbon steel substrates as measured by  
20 nanoindentation using the Nanoindenter IIs. The coating was clear and exhibited 81.2%  
21 transmission at 400 nm and 90.3% transmission at 540 nm. The coating exhibited a  
22 refractive index of 1.76 at 540 nm wavelength. The barrier properties of the coatings on  
23 the fluoropolymer and the polyethylene were measured by MOCON (Minneapolis, MN)  
24 tests using ASTM, DIN and JIS methods. The oxygen transmission rates reduced from 1.9  
25 to 80.2 times that of the uncoated substrates. The water vapor transmission rates reduced  
26 from 1.4 to 12.1 times that of the uncoated substrates.

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**Example 4**

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Cleaned four inch long ¼" OD Tygon® tubing was mounted on the bottom electrode. The tubing was mounted on two end posts so that the length of the tube was elevated and not in contact with the bottom electrode. Control samples of silicon, glass, carbon steel, and stainless steel substrates that were cleaned in a detergent, followed by Isopropanol and then blow dried with Nitrogen gas were also mounted on the substrate holder. The chamber was evacuated to an ultimate pressure of 25 mtorr. Argon gas was introduced in to the chamber to raise the pressure to 180 mtorr. An RF substrate power of 300W was used to bias the substrates for in-situ plasma cleaning. The substrates were plasma cleaned for 5 minutes. After cleaning the substrate power was ramped up to 538W which corresponded to a substrate bias of 162 V. Then the precursor was introduced through the liquid vapor delivery system. The precursor HMDSO was used in this deposition. A precursor flow rate of 0.06 g/min was used. Additional process gases such as hydrogen and oxygen were introduced simultaneously. The hydrogen flow rate was 30 sccm and the oxygen flow rate was 45.6 sccm. The deposition was performed under the above conditions for 38 minutes. The substrate holder temperature after the deposition was about 50°C. This resulted in a 0.73 micrometer thick, highly adherent coating on a flat control substrate. The coating exhibited a hardness of 6.2 GPa on carbon steel substrates as measured by nanoindentation using the Nanoindenter IIs. The coating was clear and exhibited 81.2% transmission at 400 nm and 90.3% transmission at 540 nm. The coating exhibited a strong Si-O stretching band at 1020 cm<sup>-1</sup> wavenumber, a Si-H band at around 780 cm<sup>-1</sup> and a C-H band around 2900 cm<sup>-1</sup>.

1 WE CLAIM:

- 2 1) A coating for plastic substrates comprised of carbon, hydrogen, silicon and  
3 oxygen in an amorphous structure.
- 4 2) The coating of Claim 1 comprised of a glass-like Si-O network.
- 5 3) The coating of Claim 1 comprised of a multi component structure  
6 comprising Si-O, C-H, Si-H and Si-C.
- 7 4) The coating of Claim 3 wherein Si-O and C-H are predominant.
- 8 5) The coating of Claim 1 wherein the carbon content is greater than about 25  
9 atomic percent of the coating.
- 10 6) The coating of Claim 1 wherein the carbon content is from about 25 atomic  
11 percent of the coating to about 65 atomic percent of the coating, the hydrogen content is  
12 at least about 1 atomic percent of the coating up to about 40 atomic percent of the  
13 coating, the silicon content is from about 10 atomic percent of the coating to about 30  
14 atomic percent of the coating and the oxygen content ranges from about 8 atomic percent  
15 of the coating to about 40 atomic percent of the coating.
- 16 7) The coating of Claim 1 wherein the density of the coating varies from about  
17 1.7 gm/cc to about 2.0 gm/cc.
- 18 8) The coating of Claim 1 wherein said coating is synthesized via a RF  
19 discharge plasma process.
- 20 9) The coating of Claim 1 wherein said coating is deposited by a low density,  
21 low temperature plasma enhanced chemical vapor deposition process.
- 22 10) The coating of Claim 1 wherein said coating is deposited at a temperature  
23 of or below 70°C.
- 24 11) The coating of Claim 1 wherein the coating has the properties of  
25 Nanoindentation hardness in the range of about 2 to about 10 GPa.

- 1           12)    The coating of Claim 1 wherein the coating has the properties of  
2    Nanoindentation hardness in the range of about 5 to about 7.5 GPa.
- 3           13)    The coating of Claim 1 wherein the coating has a UV transmission greater  
4    than 85% in the wavelength range of from about 360 to about 900nm.
- 5           14)    The coating of Claim 1 wherein the coating has a UV transmission greater  
6    than 90% in the wavelength range of from about 400 to about 900nm.
- 7           15)    The coating of Claim 1 wherein the coating has a surface energy of from  
8    about 27 to about 38 dyn/cm.
- 9           16)    The coating of Claim 1 wherein the coating has a water contact angle of  
10   from about 70 to about 90.
- 11          17)    The coating of Claim 1 wherein the coating has a film thickness from about  
12   50 angstroms to about 10 micrometers.
- 13          18)    The coating of Claim 1 wherein the coating is hydrophobic.
- 14          19)    The coating of Claim 1 wherein the coating is impermeable.
- 15
- 16
- 17

## AMENDED CLAIMS

[received by the International Bureau on 20 December 1999 (20.12.99);  
original claims 1,10 and 11 replaced by new claim 1 remaining  
claims unchanged (2 pages)]

- 2           1)     An abrasive resistant, transparent, barrier coating for plastic substrates  
3            comprised of carbon, hydrogen, silicon and oxygen in an amorphous structure wherein  
4            said coating is deposited at a temperature of or below about 70°C and at a pressure in the  
5            range of from about 50 mTorr to about 500 mTorr and further said coating having the  
6            properties of Nanoindentation hardness in the range of about 2 to about 10 GPa.
- 7           2)     The coating of Claim 1 comprised of a glass-like Si-O network.
- 8           3)     The coating of Claim 1 comprised of a multi component structure  
9            comprising Si-O, C-H, Si-H and Si-C.
- 10          4)     The coating of Claim 3 wherein Si-O and C-H are predominant.
- 11          5)     The coating of Claim 1 wherein the carbon content is greater than about 25  
12          atomic percent of the coating.
- 13          6)     The coating of Claim 1 wherein the carbon content is from about 25  
14          atomic percent of the coating to about 65 atomic percent of the coating, the hydrogen  
15          content is at least about 1 atomic percent of the coating up to about 40 atomic percent of  
16          the coating, the silicon content is from about 10 atomic percent of the coating to about 30  
17          atomic percent of the coating and the oxygen content ranges from about 8 atomic percent  
18          of the coating to about 40 atomic percent of the coating.
- 19          7)     The coating of Claim 1 wherein the density of the coating varies from  
20          about 1.7 gm/cc to about 2.0 gm/cc.
- 21          8)     The coating of Claim 1 wherein said coating is synthesized via a RF  
22          discharge plasma process.

- 1           9)     The coating of Claim 1 wherein said coating is deposited by a low density,  
2 low temperature plasma enhanced chemical vapor deposition process.
- 3           12)    The coating of Claim 1 wherein the coating has the properties of  
4 Nanoindentation hardness in the range of about 5 to about 7.5 GPa.
- 5           13)    The coating of Claim 1 wherein the coating has a UV transmission greater  
6 than 85% in the wavelength range of from about 360 to about 900nm.
- 7           14)    The coating of Claim 1 wherein the coating has a UV transmission greater  
8 than 90% in the wavelength range of from about 400 to about 900nm.
- 9           15)    The coating of Claim 1 wherein the coating has a surface energy of from  
10 about 27 to about 38 dyn/cm.
- 11          16)    The coating of Claim 1 wherein the coating has a water contact angle of  
12 from about 70 to about 90.
- 13          17)    The coating of Claim 1 wherein the coating has a film thickness from  
14 about 50 angstroms to about 10 micrometers.
- 15          18)    The coating of Claim 1 wherein the coating is hydrophobic.
- 16          19)    The coating of Claim 1 wherein the coating is impermeable.

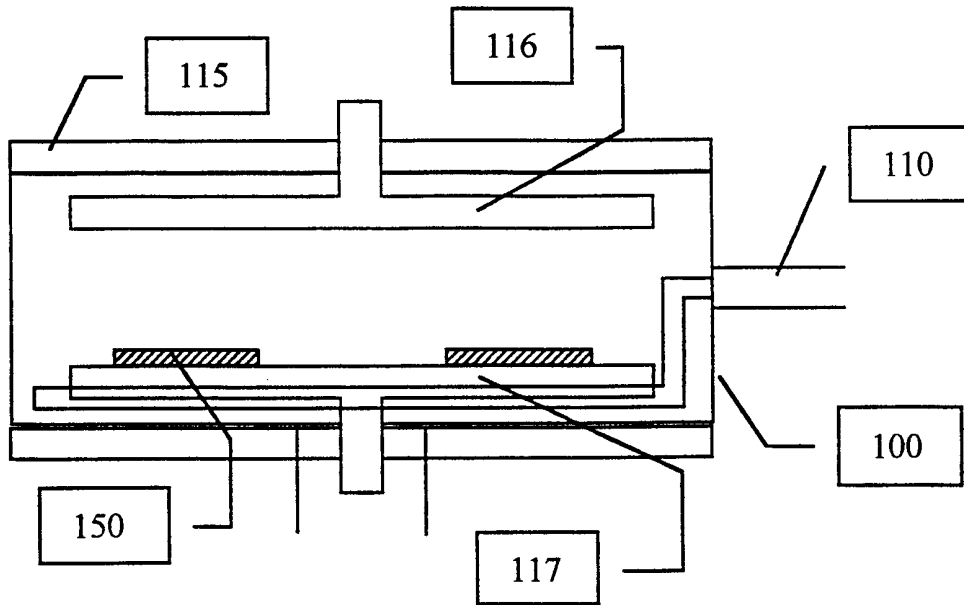


Figure 1: Schematic of a hardcoating deposition chamber.

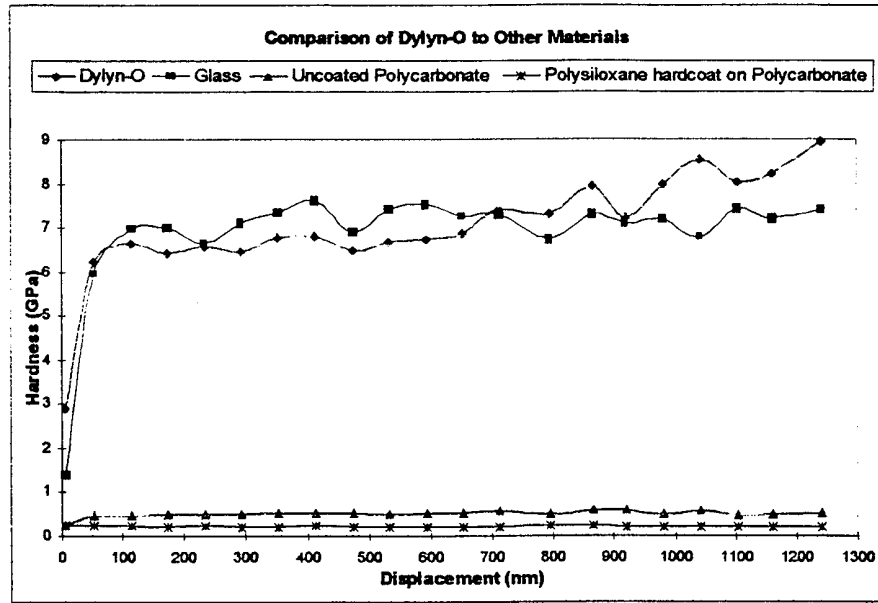


Figure 2: Comparison of Hardness of the coating with uncoated polycarbonate, bare glass and polysiloxane dip coated polycarbonate.

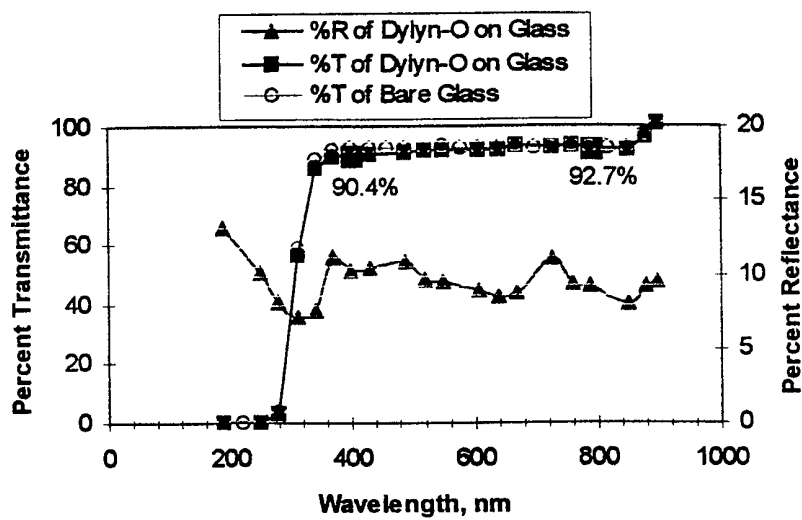


Figure 3: Typical UV-Vis transmission and reflectance spectra for a coating on glass.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/17203

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C23C 16/00; B23B 9/00

US CL :106/287.14; 428/412, 446, 447

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)

U.S. : 106/287.14; 428/412, 446, 447

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

NONE

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

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,314,724 A [TSUKUNE ET AL] 24 May 1994, see column 14, lines 5-44.	1-19
X	US 5,424,131 A [WERTHEIMER ET AL] 13 June 1995, see Table 1.	1-19
Y	US 5,508,368 A [KNAPP ET AL] 16 April 1996, see claims 16-28.	1-19
X	US 5,041,303 A [WERTHEIMER ET AL] 20 August 1991, see Table 3	1-19

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
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"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

17 SEPTEMBER 1999

Date of mailing of the international search report

19 OCT 1999

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