Diamond-Like Carbon as a protective coating for decorative glass

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Keywords

1 = Diamond-Like Carbon
2 = glass surface protection
3 = abrasion resistance
4 = corrosion resistance
5 = easy clean

Abstract

Though glass is a remarkably stable material, able to withstand most environmental stresses indefinitely without bulk failure, its surface is relatively easy to damage through mechanical contact with hard materials (e.g. glass or hardened metal) or through chemical exposure to corrosive chemicals (such as alkali solutions or certain types of hard water), leading to readily visible cosmetic defects. In as much as the ability to see through glass is one of its primary selling points, its resistance to marring, scratching or corrosion directly influences its value.

Historically, efforts to protect glass have relied on organic surface treatments or films which lower its coefficient of friction or yield under impact, or on the use of inorganic oxide or nitride coatings to produce a hard surface layer. The drawback of the organic treatments is they wear off, and of the inorganic coatings that they are easily marred due to inherently high friction. Diamond-Like Carbon is a unique material that combines the benefits of both organic and inorganic materials and thereby provides superior glass protection without wearing away.

Since its discovery in the early 1970s, the protective properties of Diamond-Like Carbon have been exploited in a diverse assortment of small-scale products, including razor blades, hard disk media, and bar-code scanner windows. This paper focuses on the development and commercialization of DLC for large area glass applications – specifically as a transparent and robust protective coating for decorative glass products.

Introduction

The need to protect glass from surface damage has been discussed extensively in the technical literature. As a relatively hard (indentation resistant) material, the brittle nature of glass not only reduces the practical strength from its theoretical limit through propagation of cracks from surface flaws, but also leads to complicated stress fields around and below the point of contact during impact, static loading and sliding contact with abrasive media, resulting in various types of surface damage and loss of optical quality [1]. The inherent chemical stability of the silica backbone enables glass to withstand most types of environmental exposure indefinitely without bulk failure, however long term exposure to a variety of organic and inorganic agents results in the gradual degradation of the appearance and cleanability, which are key features of new glass [2]. The primary culprit is roughening of the glass surface which can occur just through prolonged contact with static water through ion exchange reactions. Degradation can also occur through formation of tenacious chemical bonds with inorganic contaminants, that cannot be broken by common cleaning agents but require abrasive action; invariably contributing to surface roughness by leaving microscopic bonded residues and scratches. During installation, glass can be exposed to concrete splatter which becomes difficult to remove after hardening [3], but exposure to and precipitation of dissolved silica present in some tap water is a more obscure problem that greatly increases the maintenance effort and frequency required to keep glass clean.

Historical approaches for protecting glass have limitations, particularly when applied to decorative products such as table tops, display cabinets, shelving, mirrors and shower enclosures. Paramount for these applications is the preservation of cosmetic quality, clarity and transparency over the life of the product at a reasonable cost.

Hydrocarbon and fluorocarbon surface treatments and films have been used, in some cases to provide temporary protection from contamination during installation [3], but for the most part to generate hydrophobic properties, e.g., on automotive windshields where improved visibility in rain reduces reaction times. Under low contact loads, polymeric surface treatments can provide some protection due to low friction but with increasing load the effect is lost as the surface layer is scraped away. Further improvements in durability have been demonstrated using organic-inorganic hybrid coatings, but these are not immune to wear, even by soft materials such as wiper blades [4]. In addition, polymer based treatments must be applied in the glass shop after fabrication and thus increase labor cost and in some cases require the use of hazardous chemicals.

At the other end of the material spectrum, inorganic thin films provide limited benefit though they may be harder than glass, because the inherently high friction causes lateral contact forces to be transferred into the substrate. Accordingly, reports of improved abrasion resistance are invariably linked to friction reducing surface contaminants [5]. In cases where inorganic films are combined with organic surface treatments, e.g. on glass containers, their benefit is limited to enhancing the adhesion [6]. Real surface hardening requires either extremely hard polycrystalline ceramic coatings, which can be produced only at very high substrate temperature (or by exotic techniques such as laser sintering [7]) or extremely thick (> 1 μm) amorphous inorganic coatings [8]. In both cases cost, poor scalability, and loss of transparency make these approaches unsuitable for large area glass applications.

Carbon coatings produced by vacuum deposition

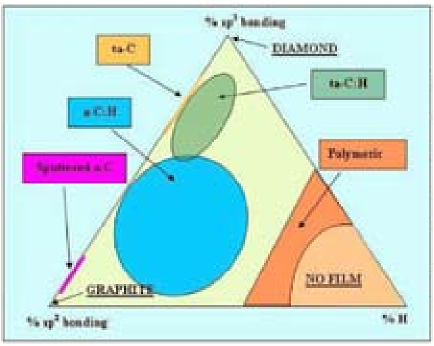
A wide variety of carbon-based coatings can be produced by vacuum processes, with a wide range of properties (Figures 1 and 2). This is a consequence of the carbon atom's unique ability to readily hybridize and form different types of covalent bonds with neighboring atoms. Carbon coating materials range from very soft graphitic or polymeric films made by evaporation or plasma polymerization, sputtered amorphous carbon (a-C) with low hardness, hard hydrogenated amorphous carbon (a-C:H) produced by biased-plasma or plasma beam, and very hard "tetrahedral" a-C or a-C:H deposited by cathodic arc sputtering or high energy ion beam deposition. Polycrystalline diamond coatings are also possible, using thermal CVD, flame CVD or microwave plasma, however high substrate temperatures are required (> 700° C). The amorphous forms of carbon are preferably grown at low temperatures (<200° C), and the also have the advantage that they resist brittle failure and can be made smoother since they have no crystalline grains.

Diamond-Like Carbon (DLC)

The term Diamond-Like Carbon, first used by Aisenberg and Chabot in 1971 [9], is used in industry today to cover amorphous carbon with a broad range of mechanical and optical properties, included both hydrogenated and non-hydrogenated forms, made with low or high energy vacuum deposition techniques.

The DLC coatings described in this paper were produced by high-energy ion-beam deposition. The beneficial properties of these coatings when applied to glass, including high mechanical hardness, low coefficient of friction, low chemical reactivity, and high transparency/neutral appearance, are a consequence of sp^3 rich carbon-carbon bonding, low (but nonzero) hydrogen content, and high mass density.

Impressive is the list of DLC applications that have either been commercialized or are in development in a wide range of industries – this includes low friction razor blades, overcoats for hard disk media and heads, durable-barcode scanner windows, biocompatible implants and surgical tools, durable high end optics, various electronic applications, and wear resistant tools [10]. However, in all cases the deposition techniques used have limited scalability. Plasma deposition (biased or not) is difficult to achieve uniformly over large areas due to electrical interactions with the substrate surface and vacuum chamber walls. The limitations of plasma beam deposition are discussed in the next section. Cathodic arc deposition is difficult to scale because the arc is in fact a small (travelling) hot spot on the cathode, and the requirement for magnetic filtering to eliminate macroparticles complicates scale-up as well. More exotic techniques such as laser ablation and mass-selected ion beam are similarly restricted.



Material	% sp^3	% H	Density (g/cm^3)	Band Gap (eV)	Hardness (GPa)
Polymeric	60-80	40-65	0.6-1.5	2-5	0.2-5
a-C:H	10-40	20-40	1.8-2.5	0.8-2.5	5-30
ta-C:H	50-75	10-20	2.7-3.0	1.5-2.5	30-60
Graphitic	0-30	0-40	1.2-2.0	0-0.6	0.2-1
a-C	5-20	0	1.8-2.2	0.5-1	5-10
ta-C	60-85	0	3.0-3.4	1.5-2.0	50-80
Diamond	100	0	3.5	5.5	100

Figure 1 and 2

Ternary plot and material properties of carbon coatings

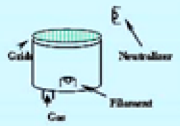
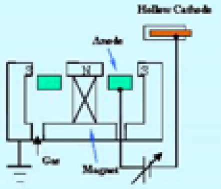
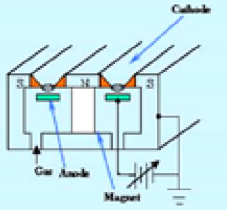
Type	Kaufman Gridded	Closed Drift	Anode Layer
			
Electron Source	Thermionic or RF-plasma	Thermionic	Cold cathode
Ion Extraction	Multiple grids	Hall effect	Hall effect
Ion Energy (eV)	50 – 1200 (narrow spread)	25 – 120 (broad)	100 – 2000 (broad)
DLC Hardness (GPa)	Up to 40	Up to 30	Up to 60
Maintenance	-	0	0
Gas utilization	0	--	•
Scalability	-	--	•

Figure 3

Types of ion sources

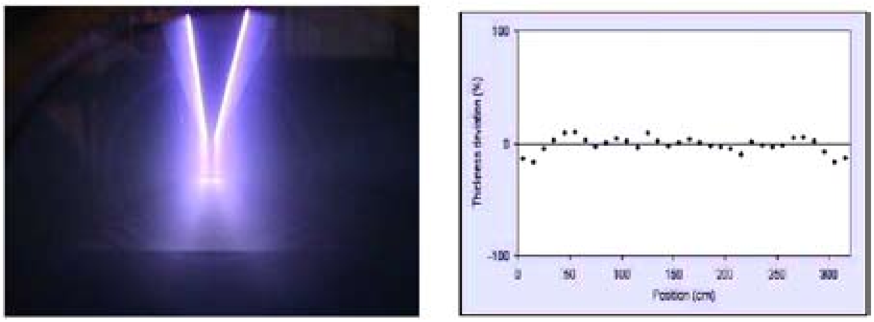


Figure 4 and 5

Anode layer source in operation and DLC thickness uniformity over the width of jumbo lite.

Ion source technologies

Ion beam processes differ from plasma deposition (also known as PECVD) in that generation and acceleration of ions occurs remotely. Hence the deposition parameters are largely decoupled from the size and shape of the substrate, and are determined by the design of the ion source instead (see Figure 3). The gridded type was pioneered by Kaufman in the USA in the 1970s, while gridless designs were concurrently developed in the former Soviet Union. In the gridded source, ion extraction and focusing is achieved by applying appropriate potentials to multiple electrostatic grids, while in the gridless designs the accelerating field is generated through interaction between the source plasma and a transversely applied magnetic field.

On the plus side, the gridded ion source provides best control of the ion beam parameters including ion energy; however the beam current is restricted due to space charge effects. The grids have limited lifetime due to ion impact erosion, and are sensitive to contamination and alignment as well. At the present time gridded ion sources have been scaled to roughly 1 meter length.

Gridless ion sources are more robust and their output is not constrained by space charge. Gridless ion sources best suited for low voltage - high current operation are the End-Hall (not shown) and the Closed-Drift types. Such beams produce diffusive plasmas that extend well beyond the ion source and hence generate "plasma beams". Ion energy and consequently the hardness of the DLC produced are limited. Scaling plasma beam sources has had little successful due to poor plasma stability/

Figure 6

Surface damage on half-coated glass, caused by repeated contact with glass and metal objects.

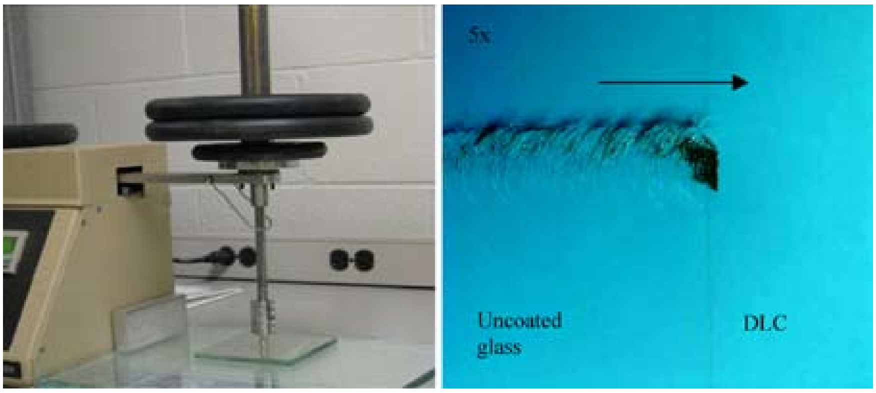


Figure 7 and 8

Basic scratch tester and scratch track on half coated sample (10 kg, 3 mm borosilicate sphere).

uniformity and due to the high gas loads require to make them run.

In contrast, the gridless anode layer source (the name refers to the compact acceleration zone near the anode) runs best at much higher voltage, producing higher beam energies and harder DLC. Good source plasma uniformity and low gas flow requirements make the anode layer source highly scalable. The DLC coatings evaluated in this paper were produced with such sources scaled up to 3.7m length. Figure 4 provides a view of the well collimated and highly uniform ion beam produce by a 3.7m ion source mounted in flat glass coater, resulting in excellent uniformity (Figure 5). The ion source is use to produce thin, dense DLC coatings on float glass, which produce high abrasion resistance and yet are highly transparent.

Benefits of DLC on glass

Many studies have been carried out to understand the extensive damage that can occur on a glass surface during contact with glass or metal objects [11]. The ability of a thin layer of DLC to protect against such damage is shown in Figure 6.

While much tribological testing is carried out using sharp microscopic indenters made of diamond, simulation of real-world contact damage requires the use of other abrader materials and geometries. Accordingly a simple abrasion tester (Figure 7) was employed to measure abrasion resistance. In this device, a sphere of a given material is dragged across a test sample with controllable speed and fixed load. The micrograph in Figure 8 depicts an abrasion track on glass partially coated with DLC, produced by a 3 mm diameter sphere made of high grade borosilicate glass with a 10 kg load. The abrader moved across the interface starting on the uncoated side where it left a pronounced scar and ending on the DLC coated side where no damage is visible.

The level of protection provided by DLC and its impact on optics is illustrated in Figure 9. The lower chart shows critical load (50% probability threshold for leaving a visible mark) and the upper chart the loss in visible transmission induced by the coating; both as a function of the DLC thickness. Comparing critical loads with abraders made of borosilicate (H ~ 6 GPa) or alumina (H ~ 40 GPa), the threshold for visible damage is less with the harder material. It should be noted however, that the critical load of clean uncoated glass is very low - with either type of abrader it is less than the 0.2 kg lower limit of the instrument. Clearly DLC can greatly improve the abrasion resistance of glass at thicknesses where its impact on transparency is low.

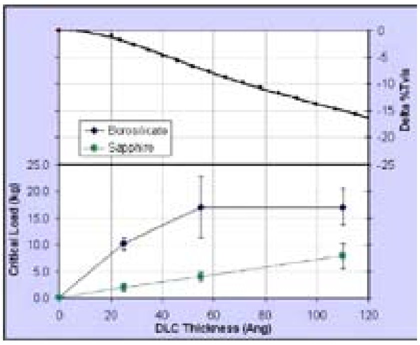


Figure 9

Critical scratch-load with 3mm borosilicate or 3mm sapphire spheres (lower) and %Tvis loss (upper) versus DLC thickness.

The high beam energy produced by the anode layer ion source also benefits adhesion. Ion implanting and ion mixing occurs during the early stage of growth which produces a transition layer that penetrates into the glass surface. Excellent adhesion keeps the DLC from scraping off during abrasion and the high hardness results in a very low wear rate. This is illustrated in Figure 10, where results from long-term durability testing are displayed. In this test a sample mounted in a reciprocating brush tester is repeatedly rubbed with a wet sponge loaded with a 1 kg weight and soaked with Soft Scrub (a common household cleaner containing calcium carbonate grit). There is a minor change in visible transmission after 10,000 strokes, indicating that a small reduction in thickness has occurred. For comparison, Figure 10 includes results for glass samples with polymeric fluorocarbon and hybrid organic-inorganic surface films. Using contact angle as an indicator, the wear rate was found to be much faster – after 600 strokes both layers were effectively gone.

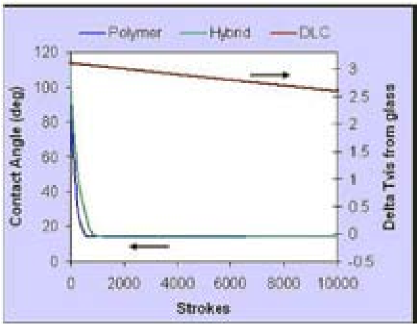


Figure 10

Long term durability test comparing polymeric and hybrid surface treatments to DLC coated glass.

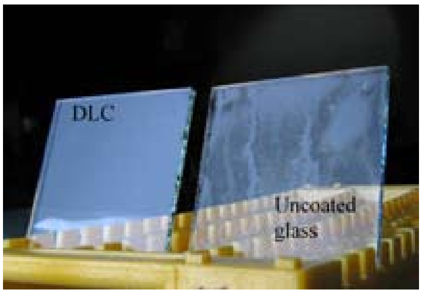


Figure 11

Stain after 10 days 50oC/95% RH

The low friction of DLC is in large part due to the chemically inert nature of this material. Its non-reactive nature provides additional benefits to glass in the form of enhanced resistance to corrosion and protection against bonding with inorganic contaminants. The ability of DLC to impede the reactions between glass and stagnant water that causes alkali leaching and ultimately roughening of the surface is shown in Figure 11, which compares DLC coated and uncoated glass after 10 day continuous exposure to 50°C and 95% RH. The DLC coating prevented the pronounced staining which occurred on the uncoated sample.

Figure 12

Half-coated glass panel after 1.5 years in a shower.

Protection against the type of damage that can occur during prolonged exposure to hard water is shown in Figure 12. Installed 18 months in a shower stall, the half-coated panel has severe and irreparable water spotting on the uncoated half, while the DLC coated area is clean. The picture shows the panel after it was cleaned – the coated side with soap and water, the uncoated additionally with household vinegar. Generally, organic acids are able to dissolve the alkali salts (calcium and magnesium carbonates) contained in hard water spots, but the tap water this panel was exposed to contained dissolved silica. Chemically similar to the surface of glass with stain, the hazy, residual surface film consists of porous silica that precipitate from drying water droplets and formed permanent bonds with the unprotected glass. Attempts to remove this film with abrasive cleaners were fruitless.

Summary

The Diamond-Like Carbon coatings presented in the paper are uniquely suited for providing lasting protection to decorative glass products such as table tops, display cabinets, shelving, mirrors and shower enclosures (examples shown in Figure 13). Applied by robust linear ion sources which have been integrated into large area MSVD coaters these coatings have the high hardness and adhesion to float glass necessary to protect against the contact damage such products typically are subjected to, without inducing a significant optical penalty. The coatings are chemically inert and consequently provide additional benefits to glass in the form of improved corrosion resistance and easy clean properties.

Acknowledgement

In memory of Mr. William Davidson, founder and owner of Guardian Industries, whose foresight and dedication made this work possible.

Figure 13

Decorative glass applications

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