3-5-93
E 7571

NASA Technical Memorandum 105943

Optical and Scratch Resistant Properties of Diamondlike Carbon Films Deposited With Single and Dual Ion Beams

Michael T. Kussmaul
Sverdrup Technology, Inc.
Lewis Research Center Group
Brook Park, Ohio

Michael S. Bogdanski
Case Western Reserve University
Cleveland, Ohio

and

Bruce A. Banks and Michael J. Mirtich
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

Prepared for the
Technology 2002 Conference
sponsored by the Technology Utilization
Baltimore, Maryland, December 1–3, 1992

NASA

OPTICAL and SCRATCH RESISTANT PROPERTIES of DIAMONDLIKE CARBON FILMS DEPOSITED WITH SINGLE and DUAL ION BEAMS

Michael T. Kussmaul
Sverdrup Technology, Inc.
Brook Park, Ohio

Michael S. Bogdanski*
Case Western Reserve University
Cleveland, Ohio

Bruce A. Banks
Michael J. Mirtich
NASA Lewis Research Center
Cleveland, Ohio

ABSTRACT

Amorphous diamondlike carbon (DLC) films were deposited using both single and dual ion beam techniques utilizing filament and hollow cathode ion sources. Continuous DLC films up to 3000 Å thick were deposited on fused quartz plates. Ion beam process parameters were varied in an effort to create hard, clear films. Total DLC film absorption over visible wavelengths was obtained using a Perkin-Elmer spectrophotometer. An ellipsometer, with an Ar-He laser (wavelength 6328 Å) was used to determine index of refraction for the DLC films. Scratch resistance,frictional and adherence properties were determined for select films. Applications for these films range from military to the ophthalmic industries.

INTRODUCTION

Extensive resources by a large number of laboratories have been dedicated to diamond film research. The attraction for diamond films is easy to understand. Diamond is the hardest known material, an excellent insulator, and has a high thermal conductivity. However, high substrate temperatures (≈ 1000°C) are required for the formation of these films. Thus, their usefulness is restricted to specialized applications and to relatively small surface areas. Hydrogenated amorphous DLC films (1) however, can be deposited at low temperatures, thus attracting numerous applications which are unapproachable by the high temperature diamond film deposition technique. DLC films can be deposited at room temperature using several plasma generating techniques as detailed by Robertson (2). With commercially available ion source systems, these deposition techniques are easily configured to coat large and/or unique samples. Ideally the only constraint regarding film deposition using ion sources is the size and pumping limitations of the vacuum facilities.

NASA Lewis Research Center and Diamonex, Inc. are performing collaborative technology development through a Space Act agreement to improve the visible wavelength transmittance of DLC films made with the dual ion beam

---

*NASA Resident Research Associate at Lewis Research Center.

system. In addition, the films must retain adequate film hardness and scratch resistance for ophthalmic applications. The goal is to develop a scratch resistant anti-reflection coating suitable for plastic lenses.

Diamondlike Carbon Film Deposition Apparatus and Procedure

Two different dual ion beam systems were used to deposit DLC films. The first system was used by Mirtich (1). It consisted of a 30 cm ion source with its grids masked down to 10 cm in diameter and an 8 cm ion source (figure 1). Argon flowed through a hollow cathode and a neutralizer to create a plasma discharge. Methane was introduced into the discharge chamber to provide a source of carbon for DLC film deposition. A second system used to deposit DLC consisted of a 15 cm diameter source and 8 cm diameter source. The 15 cm cathode filament ion source with its extraction grids masked to 10 cm diameter, is used to directly deposit DLC films using methane.

Prior to film deposition, samples are cleaned with soap solution in an ultrasonic bath, rinsed with deionized water and dried with nitrogen. The specimens to be coated are then placed in vacuum and cleaned using xenon ions at an energy of 500 eV for approximately two minutes. The total beam energy (the sum of the discharge voltage and the screen grid voltage) is kept at approximately 125 eV. Current densities at these conditions are approximately 60 $\mu a/cm^2$ in the vicinity of the sample. The deposition rate of the DLC films on fused quartz is approximately 71 Å/min.

Robertson and O'Reilly (3) have shown that a mixture of sp^2 (trigonal bonding associated with graphite) and sp^3 (tetrahedral bonding characteristic of diamond) form into graphitic clusters which are then bonded into a larger sp^3 matrix. It was also shown that the sp^2 clusters control the electronic properties in the DLC film while the sp^3 bonding is responsible for its mechanical properties. Angus and Wang (4) also discuss the role of atomic hydrogen content in DLC films as a method of increasing the sp^3 coordination while reducing the sp^2 bonding.

Mirtich, et al. (5) showed that a dual ion beam system with energetic argon ions in the second ion source could produce clearer DLC films than possible with a single ion direct deposition source. During dual-beam depositions an 8 cm cathode filament ion source with its extraction grids masked to 1 cm, is used to direct a beam of hydrogen ions, argon or xenon ions at the substrate. The current density due to hydrogen ions ranged from 80-300 $\mu a/cm^2$.

Optical Properties of Films

The spectral transmittance and reflectance of the DLC films deposited on fused quartz were obtained using a Perkin-Elmer lambda 9 spectrophotometer. The spectral absorptance is calculated based on the measured transmittance and reflectance. Figure 2 shows the transmittance for DLC films deposited with both the single and dual ion beam systems. The transmittance of the DLC film deposited with the dual ion beam system is greater for all wavelengths compared to the single beam film. A 500 Å thick film also is 90% transmitting at wavelengths greater than 7000 Å.

Figure 3 shows the results of various techniques which were tested in an effort to increase the DLC film transmittance at a wavelength of 5000 Å. The values represent the transmittance at 5000 Å (which approximates the peak sensitivity of the human eye (6)) for DLC films on fused quartz substrate for various dual beam gaseous deposition conditions. The 30 cm source for conditions 1 through 4 used a hollow cathode to produce a plasma of Argon and Methane for DLC film deposition. If the hollow cathode is replaced by a filament cathode the need to use Argon in the operation of the ion source during the DLC deposition process is eliminated. The improvement in DLC film transmittance as a result of this alteration is shown in condition 5 (Figure 3). Clearly a higher transmittance results when the dual beam system is used, and especially when hydrogen gas is used in the second source. The use of a pure hydrogen ion beam in the 8 cm ion source produced a DLC film with a transmittance of 84%.

Index of refraction measurements were made with an Ellipsometer II system manufactured by Applied Materials, Inc.. This system uses a 2 milliwatt helium-neon laser, with a wavelength of 6328 Å and at a 70° angle of incidence with the surface. This ellipsometer produces data which is used to calculate both the index of refraction and the film thickness. The calculated film thickness is compared to the value obtained using a Dektak surface profilometer to determine the reliability of the calculated index of refraction. The techniques showed agreement within approximately 70 Å.

A DLC film's index of refraction is important because this property determines the required film thickness for use in an anti-reflective stack coating. As the difference between two materials' indices of refraction increases, less of each material is required to produce an anti-reflective coatings. This smaller amount of material (thinner film) would correspond to a higher transmittance because of less light attenuation and to a reduction in film deposition time. both of these factors (less material, less time) translate to a lower cost to produce anti-reflective coatings.

The DLC films made with the direct deposition technique using methane in a single ion source produce films which have an index of refraction of 2.0. When a hydrogen beam is directed at the sample during film deposition the index of refraction decreases to values of 1.75 to 1.8 as the current density of the hydrogen beam in the second ion source is increased.

SCRATCH RESISTANCE and ADHERENCE

Diamond stylus scratch tests were performed on both a DLC coated and an uncoated fused quartz plate. The DLC coating had a thickness of 1650Å, and was deposited using a single ion beam source. The plates were ultrasonically cleaned in acetone, rinsed with pure ethanol followed by deionized water, then dried in air. A diamond stylus with a hemispherical radius of 841 μm was slid along the plate at a rate of 10 mm/min. A progressive normal load of 0 to 25N was applied at a rate of 100 N/min. These parameters generated a total scratch length of 2.5 mm with an effective load-displacement relationship of 10 N/mm. The frictional force and acoustic emission were monitored during the scratch tests. The acoustic emission signal is an accurate indicator as to when fracture initiates for brittle materials, such as fused quartz.

Figure 4 summarizes the results from the scratch tests on the coated and uncoated plates. The acoustic emission signal indicates that fracture initiated on the uncoated quartz plate began to fracture at approximately 13 N normal load whereas the DLC coated plate did not begin to fracture until approximately 21 N normal load. The frictional force was relatively linear in both cases, but was notably lower for the coated plate. The average friction coefficient (frictional force divided by normal force) for the test duration was 0.04 ±0.01 for the uncoated plate and 0.03 ±0.01 for the DLC coated plate.

This reduction in friction is the most likely reason that the DLC coated plate withstood a higher normal load before fracturing than the uncoated plate. A spherical stylus sliding along a flat plate generates a maximum tensile stress at the trailing edge of the sliding contact (7). It has been shown that this trailing edge tensile stress is the cause of failure in brittle materials (ref 9). This tensile stress is amplified by the friction coefficient between the stylus and the plate. Therefore a reduction in friction coefficient also reduces the tensile stress at the trailing edge of the contact.

Abrasion tests were performed on single ion beam DLC films deposited on fused quartz by rubbing SiO_2 particles (≈ 80 μm particle size) over the surface. These particles were rubbed on the surface by hand. Figure 5 shows how the DLC film coated side was protected from the abrasive particles while scratches can be seen on the uncoated portion of the sample.

Adherence of DLC films deposited on fused quartz using both the single and dual beam methods was measured by Mirtich (10). The adherence of these films were as good as the maximum adherence of the Sebastian Adherence Tester used to make the measurement (5.5×10^7 N/m^2 or 8000 psi), regardless of the method of deposition. The film adherence was so great in fact that often portions of the quartz lifted off leaving the DLC film intact.

Potential DLC Applications

A variety of companies in the United States were surveyed in 1989 by the regarding the potential commercial applications of DLC films. Table I lists the 12 applications which were most highly rated of the 39 questionnaire responses received. In addition, Table II lists of the focussed applications which are being explored at NASA Lewis Research Center and Diamonex, Inc. for which DLC films would be well suited.

Summary

DLC films are hard, very adherent and can be deposited at room temperature. These films may prove to be beneficial in technological areas seeking to improve the scratch resistance of materials through the use of novel thin coatings. The availability of ion beam systems (whether dual or single beam) facilitates configuring systems for deposition onto large, non-standard shapes. Single beam DLC films are already being used as scratch resistant coatings on sunglass lenses which are available commercially since high transparency is not as critical. The addition of a second ion source has been shown to improve film transmittance, thus increasing the usefulness of these films to other eyewear and optical surfaces (automotive windows, scanners, etc.). The index of refraction for DLC films is reduced when a dual ion system employing a hydrogen beam is used. A DLC coated quartz plate has shown a superior ability to resist fracture under sliding in comparison to an uncoated quartz plate. Thus, the use of a fairly thin DLC film has the potential to provide improved scratch resistance beyond the capability of the substrate onto which it is deposited.

REFERENCES

1. Mirtich, M.J.; Swec, D.M.; and Angus, J.C.: Dual-Ion-Beam Deposition of Carbon Films with Diamond-Like Properties. Thin Solid Films, vol. 131, 1985, pp. 245-254.

2. Robertson, J.: Properties of Diamond-Like Carbon. Surf. Coat. Technol., vol. 50, 1992, pp. 185-203.

3. Robertson, J.; and O'Reilly, E.P.: Electronic and Atomic Structure of Amorphous Carbon. Phys. Rev. B, vol. 35, 1987, pp. 2946-2957.

4. Clausing, R.E.: Diamond and Diamond-Like Films and Coatings, NATO Advanced Study Institute Series B: Physics, Vol. 266, Plenum, New York, 1991.

5. Mirtich, M.J.; Swec, D.M.; and Angus, J.C.: Dual Ion Beam Deposition of Carbon Films With Diamondlike Properties. NASA TM-83743, 1984.

6. American National Standard for Ophthalmics-Nonprescription Sunglasses and Fashion Eyewear Requirements. Sept. 25, 1986.

7. Boresi, A.P.; and Sidebottom, O.M.: Advanced Mechanics of Materials. Fourth ed., John Wiley & Sons, New York, 1985.

8. Bull, S.J.: Failure Modes in Scratch Adhesion Testing. Surf. Coat. Technol., vol. 50, 1991, pp. 25-32.

9. Mirtich, M.J.: Adherence of Ion Beam Sputter Deposited Metal Films on H-13 Steel. J. Vac. Sci. Technol., vol. 18, no. 2, Mar. 1981, pp. 186-189.

TABLE I
POTENTIAL DIAMONDLIKE CARBON FILM APPLICATIONS

DLC Film Application	Desirable DLC Film Properties
1. Protective coating for sunglass lenses	Hardness, scratch resistance
2. Protective coating for eyeglass lenses	Hardness, scratch resistance, transmittance
3. Hermetic coating for eyewear	Hermeticity, hardness, scratch resistance, transmittance
4. Abrasion, moisture resistent coating for optical surfaces (visible and infrared)	Hermeticity, hardness, scratch resistance, transmittance
5. Magnetic recording head	Hermeticity, hardness, scratch resistance
6. Coating computer hard disk	Hermeticity, hardness, scratch resistance
7. Abrasion resistant coating for optical windows in bar code scanners	Hardness, scratch resistance
8. Biomedical applications	Biocompatibility, hermeticity
9. Chemically resistant protec tive coating	Hermeticity, hardness
10. Enhanced IR transmittance of Ge and Si Infrared optics	IR transmittance, index of refraction, abrasion protection
11. Cutting blades	Smoothness, hardness, hermeticity
12. Abrasion resistant non-stick coating for cookware	Hardness, scratch resistance

TABLE II

FOCUSED DIAMONDLIKE FILM APPLICATIONS AT NASA LEWIS RESEARCH CENTER

(1) Abrasion-Resistant Anti-Reflective Optical Coatings

- Plastic sunglass lenses
- Plastic eyeglass lenses
- Other optical substrates such as glass

(2) Chemical/environmental protection ("hermetic sealing") of transparent substrates

- Quartz
- Glass
- Plastics

(3) Wear Protection of Non-Optical Substrates

- Magnetic Disks
- Cutting Surfaces
- Other Wear Parts

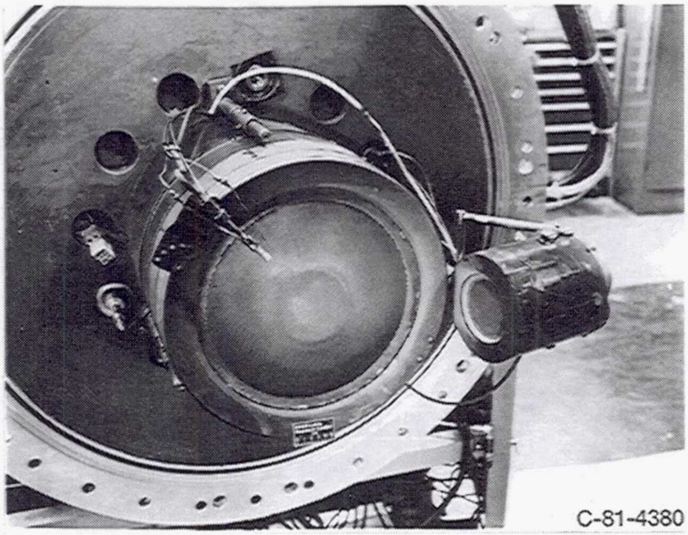

Figure 1.—Photo of dual ion beam apparatus.

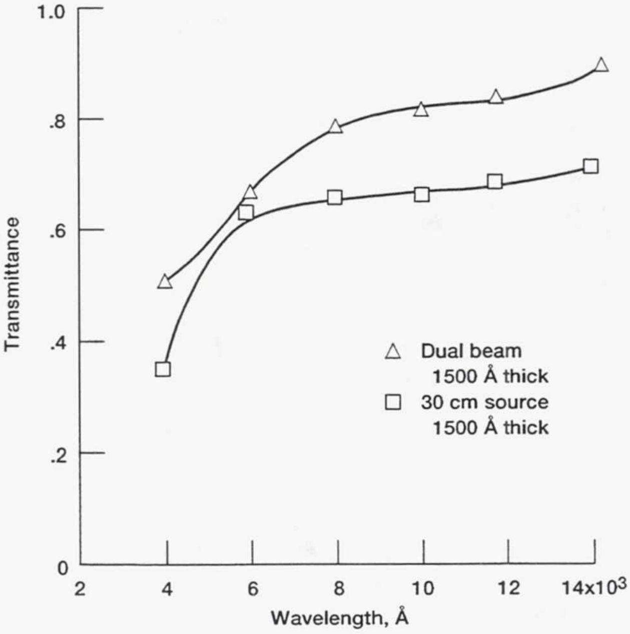

Figure 2.—Transmittance versus wavelength for DLC films using CH_4 in dual beam or single ion sources.

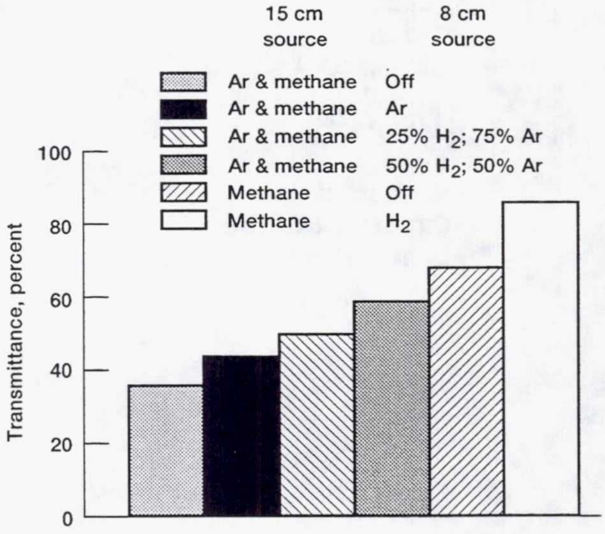

Figure 3.—Transmittance at 0.5 µm for 1000 Å thick DLC films deposited on quartz under various dual beam conditions.

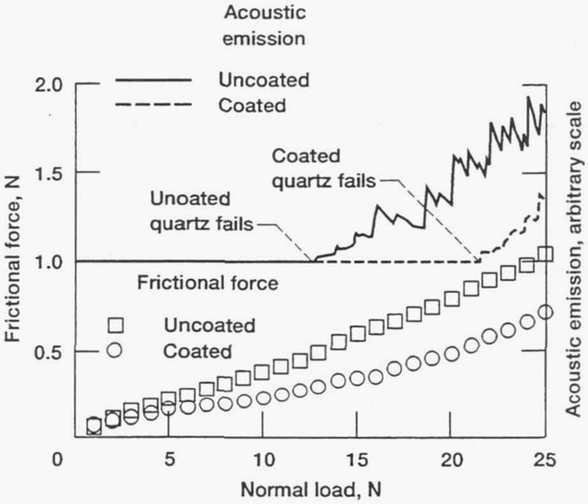

Figure 4.—Coated quartz shows lower friction and withstands higher normal load before fracture (as indicated by acoustic emission).

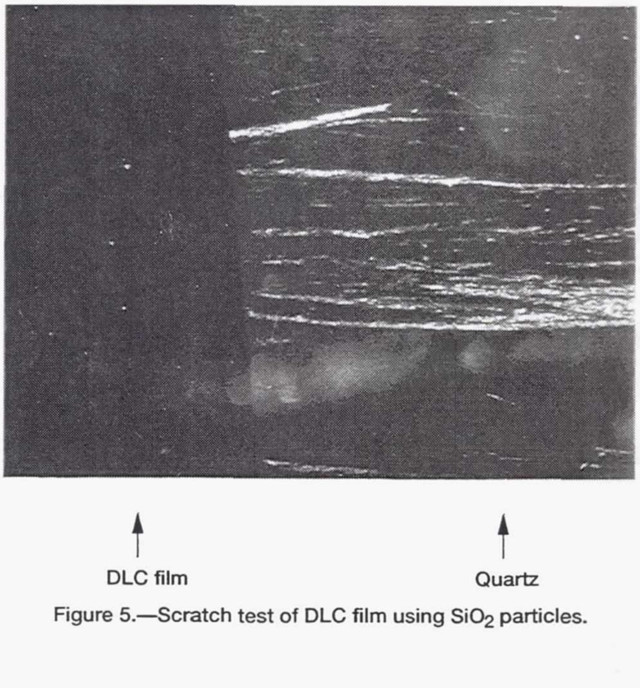

Figure 5.—Scratch test of DLC film using SiO_2 particles.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	**2. REPORT DATE** January 1993	**3. REPORT TYPE AND DATES COVERED** Technical Memorandum

4. TITLE AND SUBTITLE

Optical and Scratch Resistant Properties of Diamondlike Carbon Films Deposited With Single and Dual Ion Beams

5. FUNDING NUMBERS

WU–141–20–OJ

6. AUTHOR(S)

Michael T. Kussmaul, Michael S. Bogdanski, Bruce A. Banks, and Michael J. Mirtich

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E-7571

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM–105943

11. SUPPLEMENTARY NOTES

Prepared for the Technology 2002 Conference, sponsored by the Technology Utilization, Baltimore, Maryland, December 1–3, 1993. Michael T. Kussmaul, Sverdrup Technology, Inc., Lewis Research Center Group, 2001 Aerospace Parkway, Brook Park, Ohio 44142; Michael S. Bogdanski, Case Western Reserve University, Cleveland, Ohio 44106; and Bruce A. Banks and Michael J. Mirtich, NASA Lewis Research Center, Cleveland, Ohio. Responsible person, Michael T. Kussmaul, (216) 433–8036.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 23

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

Amorphous diamondlike carbon (DLC) films were deposited using both single and dual ion beam techniques utilizing filament and hollow cathode ion sources. Continuous DLC films up to 3000 Å thick were deposited on fused quartz plates. Ion beam process parameters were varied in an effort to create hard, clear films. Total DLC film absorption over visible wavelengths was obtained using a Perkin-Elmer spectrophotometer. An ellipsometer, with an Ar-He laser (wavelength 6328 Å) was used to determine index of refraction for the DLC films. Scratch resistance, frictional and adherence properties were determined for select films. Applications for these films range from military to the ophthalmic industries.

14. SUBJECT TERMS

15. NUMBER OF PAGES

10

16. PRICE CODE

A03

17. SECURITY CLASSIFICATION OF REPORT Unclassified	**18. SECURITY CLASSIFICATION OF THIS PAGE** Unclassified	**19. SECURITY CLASSIFICATION OF ABSTRACT** Unclassified	**20. LIMITATION OF ABSTRAC**

National Aeronautics and
Space Administration

Lewis Research Center
Cleveland, Ohio 44135

NASA