Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

TITLE: CHARACTERIZATION AND PERFORMANCE OF CARBON FILMS
DEPOSITED BY PLASMA AND ION BEAM BASED TECHNIQUES

AUTHOR(S): Kevin C. Walter M. Nastasi
H. Kung J. Koskinen
T. Levine J-P. Hirvonen
J.T. Tesmer
P. Kodali
B.P. Wood
D.J. Rej

SUBMITTED TO: 1994 Fall Materials Research Society Symposium
Proceedings

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CHARACTERIZATION AND PERFORMANCE OF CARBON FILMS DEPOSITED BY PLASMA AND ION BEAM BASED TECHNIQUES

K.C. Walter*, H. Kung*, T. Levine*, J.T. Tesmer*, P. Kodali*, B.P. Wood*, D.J. Rej*, M. Nastasi*, J. Koskinen** and J-P. Hirvonen**

*Los Alamos National Laboratory, MS-K762, Los Alamos, NM 87545

**VTT Manufacturing Technology, Materials Technology, P.O. Box 1703, FIN-02044 VTT, Finland

ABSTRACT

Plasma and ion beam based techniques have been used to deposit carbon-based films. The ion beam based method, a cathodic arc process, used a magnetically mass analyzed beam and is inherently a line-of-sight process. Two hydrocarbon plasma-based, non-line-of-sight techniques were also used and have the advantage of being capable of coating complicated geometries. The self-bias technique can produce hard carbon films, but is dependent on rf power and the surface area of the target. The pulsed-bias technique can also produce hard carbon films but has the additional advantage of being independent of rf power and target surface area. Tribological results indicated the coefficient of friction is nearly the same for carbon films from each deposition process, but the wear rate of the cathodic arc film was five times less than for the self-bias or pulsed-bias films. Although the cathodic arc film was the hardest, contained the highest fraction of sp^3 bonds and exhibited the lowest wear rate, the cathodic arc film also produced the highest wear on the 440C stainless steel counterface during tribological testing. Thus, for tribological applications requiring low wear rates for both counterfaces, coating one surface with a very hard, wear resistant film may detrimentally affect the tribological behavior of the counterface.

INTRODUCTION

A number of methods have been devised to deposit carbon-based films since the first reported fabrication of diamond-like carbon or DLC^{1,2}. Deposition methods and corresponding film properties for many types of carbon-based films have been reviewed³⁻⁹. Indeed, extensive research of deposition methods and film properties have led to the classification of carbon-based films into categories defined by both synthesis method and film composition. DLC films in particular are attracting interest due to their relatively simple fabrication, high hardness⁵, low coefficients of friction and wear rates against a number of materials⁹⁻¹⁷ and chemical inertness^{6,13,17}.

This work compares the tribological behavior of carbon films generated by three different processes. The cathodic arc process is inherently a line-of-sight ion beam process, especially if magnetic mass analysis is used to filter out large particles from the deposition beam. Cathodic arc processes depend on an electrical arc between graphite electrodes to generate carbon ions, and due to the inherent ion energy distribution of the arc and superior film properties, the carbon is deposited with energies less than 100 eV. The self-bias method is a hydrocarbon plasma-based process that relies on a combination of rf-power and the ratio of target to vacuum chamber wall (the electrodes) areas to define the magnitude of the self-bias on the target. In

general, the self-bias process uses gas pressures greater than 1 mtorr and deposits molecular ions with energies greater than 100 eV. The cathodic arc and rf-plasma self-bias techniques have been studied extensively³⁻¹⁷. In addition, carbon films have been deposited using a rf plasma-based, pulsed-bias process. Like the self-bias method, the pulsed-bias method is a non-line-of-sight process and thus lends itself to deposition onto geometrically complicated surfaces. The pulsed-bias method has the additional advantage of the bias being independent of the area of the target. Because of this area independence, it is possible the pulsed-bias method could be scaled up to perform simultaneous deposition over many square meters. The pulsed-bias process¹⁸ uses hydrocarbon gas pressures greater than 1 mtorr and deposits molecular ions with energies greater than 1000 eV. A comparison between hydrogenated and hydrogen free carbon films has been made¹⁹ but did not include carbon films made using a pulsed-bias method.

EXPERIMENTAL DETAILS

The cathodic arc process²⁰ utilized a pulsed 60 eV, $^{12}\text{C}^+$ beam extracted from a cathodic arc discharge between graphite electrodes. The deposition rate on D3 tool steel was $\sim 1 \mu\text{m/hr}$. Another carbon film was deposited on silicon from an 13.56 MHz rf-generated CH_4 (4.6 mtorr) plasma and 450 V self-bias. The deposition rate was $\sim 0.1 \mu\text{m/hr}$. The carbon film deposited by the pulsed-biased method used a C_2H_2 rf-plasma (1.2 mtorr), a negative pulse-bias of -21 kV, a pulse frequency of 2 kHz, and a pulse width of 20 μs . The deposition rate, on silicon, was $\sim 0.2 \mu\text{m/hr}$. Film thicknesses are shown in Table I.

High energy resonant ion back-scattering, to determine the carbon atom content of the films, was accomplished using a 3.55 MeV $^4\text{He}^+$ beam, 70-90 nA beam current, normal incidence, 166° scattering angle and 20 μC collected charge. These conditions were chosen to take advantage of the 6.5x increase in carbon sensitivity when using a 2 MeV $^4\text{He}^+$ beam²¹. Elastic Recoil Detection (ERD) analysis was achieved using an identical beam, except the beam was incident on the surface at 75° with a scattering angle of 30° , beam current of 4-7 nA and 4 μC collected charge. The back-scattered and ERD spectra were quantitatively analyzed using conventional computer-aided techniques²².

Cross-sectional transmission electron microscopy (XTEM) specimens were examined by conventional TEM and SAD methods using a 300 kV electron beam. In addition, parallel electron energy loss spectroscopy (PEELS) spectra were collected using a GATAN PEELS system mounted on the electron microscope. The energy resolution of the PEELS spectra is ~ 1 eV, as estimated from the full-width at half-maximum of the zero-loss peak. The EELS spectra shown here are only of the carbon K-edge after background subtraction.

Nanoindentation tests were conducted using a Nano Indenter[®] II²³. The hardness and elastic modulus of the films was calculated (with elastic corrections) from load /displacement curves at various depths. Average values and standard deviations were calculated from the ten measurements of hardness and elastic modulus at each depth.

Pin-on-disk (POD) tribological tests were conducted using 6 mm diameter 440C stainless steel pin and a load of 0.8 N. The contact stress on the cathodic arc film was 829 MPa, 539 MPa on the self-bias film, and 457 MPa on the pulsed-bias film. The yield stress of 440C is 450 MPa. The track diameter was ~ 3 mm, the sliding speed was ~ 35 mm/sec, and the total sliding distance was ~ 1.1 km. After testing, the wear track cross-sectional area was measured by surface profilometry at four positions around the track, each about 90° apart. The largest observed cross-sectional area was used to calculate the wear track volume. Wear rates were

calculated using the methodology of Holmberg and Matthews²⁴. During the wear test, the coefficient of friction was continuously monitored using a calibrated load cell.

RESULTS

The results of quantitative analysis of the high energy resonance ion backscattering and ERD spectra are shown in Table I. Film thickness, from surface profilometry measurements, and composition information were combined to calculate the mass density and the gram-atom number density⁶ for each of the films.

TABLE I. Carbon film composition, thickness, and density.

Deposition Process	at% C ± 3 at%	at% H ± 3 at%	Thickness (μm)	Mass Density (g/cm^3)($\pm 25\%$)	Gram-atom Density ($\text{g-at}/\text{cm}^3$)($\pm 25\%$)
Cathodic Arc	> 99.5	< 0.5	0.80	2.5	0.21
Self-bias	61	39	0.52	2.5	0.30
Pulsed-bias	74	26	0.66	2.7	0.32

The TEM and SAD results indicated the films were amorphous and homogeneous. PEELS spectra for amorphous carbon standard and the three carbon films are shown in Fig. 1. The sp^3 contents were calculated from the spectra using the method of Berger and McKenzie²⁵, which is based on a comparison of the area of the π^* peak relative to the remainder of the carbon K-edge energy loss spectra for an amorphous carbon sample consisting of 100% sp^2 bonding, with a carbon sample containing an unknown fraction of sp^2 bonding. Assuming sp^1 bonding is absent; $\%\text{sp}^3 = 100 - \%\text{sp}^2$. Multiple scattering was taken into account when calculating the sp^3 content. The error in the sp^3 content is ± 5 -10%. The amorphous carbon standard, which represents 100% sp^2 bonding, was a holey carbon film on a TEM grid.

Nanoindentation test indicates the cathodic arc carbon film is the hardest at 42 GPa and has an elastic modulus of 430 GPa ($\sim 40\%$ of diamond⁵). The carbon film deposited by the self-bias method has a hardness of 11 GPa and an elastic modulus of 100 GPa. To put the nanoindentation results in perspective, silicon has hardness of 10 GPa and an elastic modulus of 73 GPa. The carbon film deposited using the pulsed-bias method had a hardness of 9 GPa and an elastic modulus of 80 GPa.

Tribological testing indicated the coefficient of friction is virtually independent of the film process and varies slightly between 0.08 and 0.14 during testing. However, the wear rates differ up to a factor of five. The cathodic arc carbon film exhibited the lowest wear rate at $0.06 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The self-bias film had a wear rate of 0.32×10^{-6} and the pulsed-bias film had a wear rate of $0.27 \times 10^{-6} \text{ mm}^3/\text{Nm}$. All wear rates have errors of $\pm 7\%$. In addition, the wear scars on the 440C stainless steel pins were examined using an SEM. Because of the films high hardness, the pin worn against the cathodic arc film exhibited noticeably more wear than either of the pins worn against the other softer films.

DISCUSSION

Carbon-based films have been reported to have a wide range of compositions and properties³⁻⁵. Hydrogenated amorphous carbon-based films, such as those deposited by the self-bias and pulsed-bias methods, are generally referred to as diamond-like carbon (DLC) films⁴ if the sp^3 content is between 30 and 60%, the hydrogen content is between 10 and 40% and have hardness values between 10 and 40 GPa. Non-hydrogenated amorphous carbon-based

Fig. 1a. Carbon K-edge electron energy loss spectrum for the a-carbon standard.

Fig. 1b. Carbon K-edge electron energy loss spectrum for the cathodic arc film.

Fig. 1c. Carbon K-edge electron energy loss spectrum for the pulsed-bias film.

Fig. 1d. Carbon K-edge electron energy loss spectrum for the self-bias film.

films, such as deposited by the cathodic arc method, are referred to as diamond-like⁴ because of their high hardness (30-130 GPa), high sp^3 contents (85-95%) and low hydrogen content (<1at%). For each of the deposition methods included in this study, the composition and

properties lend credence to referring to these carbon based films as hydrogenated and non-hydrogenated DLC films.

The hardness of the carbon films is dependent on sp^3 content and deposition process. Noting that the sp^3 contents of the self-bias and pulsed-bias films are similar, the pulsed-bias film may be softest because of graphitization, caused by radiation damage within the collision cascade of the 21 kV incident ions during deposition^{3,26}. Due to the details of the deposition process, the cathodic arc film has the highest sp^3 content and, thus, the highest hardness.

The very low friction coefficients (0.08-0.14) exhibited in this work are in good agreement with that reported for cathodic arc DLC films⁹ as well as other tribological studies¹⁰⁻¹⁷, where μ varies between 0.02 and 0.25, including DLC deposited from a variety of methods. The general trend of the film wear rate decreasing²⁷, and the pin wear increasing, with film hardness is also consistent with the tribological behavior of other material systems.

CONCLUSIONS

Each tribological application of DLC films should be evaluated carefully and wear rate criteria should be established for both the DLC film and its counterface. Although the high hardness and low wear rate of the cathodic arc film may at first seem desirable, the detrimental effect such a film can have on a sliding counterface should not be ignored. Generally speaking, wear debris generation from either surface could diminish the tribological lifetime of the whole system. Even though the wear rates for the self-bias and pulsed-bias films are five times higher than the wear rate for the cathodic arc film, the wear on the 440C counterface was noticeably less. In practice, a tribological system consisting of a pulsed-bias film and a 440C counterface may therefore outperform a similar system employing a cathodic arc film. Because of their high hardness, DLC films deposited using a cathodic arc process may be best suited for situations where erosive wear is the dominant wear mechanism and there is no counterface involved. In contrast, softer and less wear resistant DLC films deposited from self-bias or pulsed-bias processes may be more suitable for applications suffering from abrasive or adhesive wear and counterface wear is a consideration.

If a DLC film is used for a tribological application, an economical deposition process should be chosen. The choice should be based on required film properties, details of the tribological problem, and the amount of area requiring a coating. This work has demonstrated that a pulsed-bias process, which is area-independent and may be capable of coating complicated geometrical shapes, can be used to fabricate DLC films that, depending on the details of the application, could outperform harder and more wear resistant films deposited using other, more complicated and inflexible processes.

ACKNOWLEDGMENTS

This work was partially supported by the United States Department of Energy Office of Basic Energy Science, Division of Materials Science. We gratefully acknowledge the technical assistance of Ivars Henins, Mark Hollander, and Caleb Evans. All ion beam analysis was performed at the Ion Beam Materials Laboratory at the Los Alamos National Laboratory.

BIBLIOGRAPHY

1. H. Schmellenmeier, Z. Phys. Chem. **205**, 349 (1955/56).
2. S. Aisenberg, R. Chabot, J. Appl. Phys. **42**, 2953 (1971).
3. J. Robertson, Prog. Solid St. Chem. **21**, 199 (1991).
4. K. Holmberg, A. Matthews, Coatings Tribology: Properties, Techniques and Applications in Surface Engineering, edited by D. Dowson, (Elsevier, Amstersdam, 1994), pg. 214-215.
5. J. Robertson, NATO ASI Series B, **266**, 331 (1991).
6. J.C. Angus, P.Koidl and Domitz, in Plasma Deposited Thin Films, edited by J. Mort, F. Jansen, (CRC Press, Boca Raton, Florida, 1986), p. 89.
7. M.W. Geis and M.A. Tamor, in Encyclopedia of Applied Physics, Vol. 5, edited by G.L. Trigg, (VCH Publishers, Inc, New York, 1991), p. 1.
8. Y. Catherine, NATO ASI Series B, **266**, 193 (1991).
9. J-P. Hirvonen, R. Lappalainen, J. Koskinen, A. Antilla, T.R. Jervis, M. Trkula, J. Mater. Res. **5**, 2524 (1990).
10. K. Enke, H. Dimigen, H. Hübsch, Appl. Phys. Lett. **36**, 291 (1980).
11. R. Wei, P.J. Wilbur, A. Erdemir, F.M. Kustas, Surf. Coat. Technol. **51**, 139 (1992).
12. K. Oguri, T. Arai, J. Mater. Res. **7**, 1313 (1992).
13. R.L.C. Wu, Surf. Coat. Technol. **57**, 258 (1992).
14. Y. Itoh, S. Hibi, T. Hioki, J. Kawamoto, J. Mater. Res. **6**, 871 (1991).
15. B. André, J-Ph. Nabot, L. Lombard, P. Martin, NATO ASI Series E, **266**, 313 (1991).
16. A. Grill, V. Patel, B.S. Meyerson, NATO ASI Series E, **266**, 417 (1991).
17. A. Antilla, in Structure-Property Relationships in Surface-Modified Ceramics, edited by C.J. McHargue, R. Kossowsky, W.O. Hofer, (Kluwer Academic Publishers, 1989), p. 455.
18. J. Chen, J.R. Conrad and R.A. Dodd, Journal of Materials Engineering and Performance **2**, 839 (1993).
19. K. Holmberg, J. Koskinen, H. Ronkainen, J. Vihersalo, J-P. Hirvonen and J. Likonen, accepted for publication in Diamond Films and Technology, 1994.
20. J-P. Hirvonen, J. Koskinen, R. Lappalainen and A. Antilla, Materials Science Forum **52/53**, 197 (1989).
21. Handbook of Modern Ion Beam Materials Analysis, edited J.T. Tesmer and M. Nastasi, (to be published by the Materials Research Society, 1995).
22. L.R. Doolittle, Nucl. Instr. Meth. **B9**, 334 (1985).
23. Nano Instruments, Inc., Knoxville, TN.
24. K. Holmberg, A. Matthews, Coatings Tribology: Properties, Techniques and Applications in Surface Engineering, edited by D. Dowson, (Elsevier, Amstersdam, 1994), p. 53.
25. S.D. Berger and D.R. McKenzie, Phil. Mag. Lett. **57**, 265 (1988).
26. Y. Lifshitz, S.R. Kasi, and J.W. Rabalais, Phys. Rev. **B41**, 10468 (1991).
27. B. Bhushan, B.K. Gupta, Handbook of Tribology: Materials, Coatings, and Surface Treatments, (McGraw-Hill, New York, 1991), p. 3.30.