ANL/CHM/CP--86016
Conf-950454--5

Physical and Tribological Properties of Diamond Films

Grown in Argon-Carbon Plasmas*

C. Zuiker, A. R. Krauss, D. M. Gruen, X. Pan, J. C. Li, R. Csencsits,
A. Erdemir, C. Bindal, G. Fenske

Materials Science, Chemistry, and Energy Technology Divisions
Argonne National Laboratory, Argonne, IL 60439

Submitted for the Proceedings of the
1995 International Conference on Metallurgical Coatings and Thin Films
Symposium on the Synthesis and Characterization of
Diamond and Related Materials
San Diego, California

April 24-28, 1995

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.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under contract W-31-109-ENG-38.

DISCLAIMER

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

Physical and Tribological Properties of Diamond Films Grown in Argon-Carbon Plasmas*

C. Zuiker, A. R. Krauss, D. M. Gruen, X. Pan, J. C. Li, R. Csencsits, A. Erdemir, C. Bindal, G. Fenske

Materials Science, Chemistry, and Energy Technology Divisions, Argonne National Laboratory, Argonne, IL 60439

Nanocrystalline diamond films have been deposited using a microwave plasma consisting of argon, 2-10% hydrogen and a carbon precursor such as C_{60} or CH_4 . It was found that it is possible to grow the diamond phase with both carbon precursors, although the hydrogen concentration in the plasma was 1-2 orders of magnitude lower than normally required in the absence of the argon. Auger electron spectroscopy, x-ray diffraction measurements and transmission electron microscopy indicate the films are predominantly composed of diamond. Surface roughness, as determined by atomic force microscopy and scanning electron microscopy indicate the nanocrystalline films grown in low hydrogen content plasmas grow exceptionally smooth (30-50 nm) to thicknesses of 10 μm . The smooth nanocrystalline films result in low friction coefficients ($\mu=0.04-0.06$) and low average wear rates as determined by pin-on-disk measurements.

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under contract W-31-109-ENG-38.

1. Introduction

Research in the area of diamond thin film deposition has increased significantly in the last ten years. The remarkable properties of diamond including its extreme hardness, low coefficient of friction, chemical inertness, high thermal conductivity, transparency and semiconducting properties make it attractive for a number of applications.^{1,2,3} The high hardness and low coefficient of friction of natural diamond make diamond films good prospects for tribological applications. Friction and wear properties have been investigated for the case of diamond and various other materials sliding against diamond films.^{4,5,6,7} The friction coefficient has been directly related to the surface roughness of the films, with smoother films approaching the reported value for natural diamond.^{8,9,10}

In this paper, we focus on nanocrystalline diamond films deposited using a microwave plasma consisting of argon, 2-10% hydrogen and a carbon precursor such as C₆₀ or CH₄. It was found that it is possible to grow the diamond phase with all three carbon precursors, although the hydrogen concentration in the plasma was 1-2 orders of magnitude lower than normally required in the absence of the argon. A variety of techniques are used to characterize the composition and surface of these films. Friction and wear measurements are performed to characterize the tribological properties of the films

2. Experimental Technique

2.1 Film Deposition

Diamond films were deposited in a microwave plasma chemical vapor deposition reactor (ASTeX PDS-17) as previously described.^{11,12} The films were grown on single crystal silicon wafers polished with 0.1 μm diamond particles to enhance nucleation density. Film growth was monitored in situ using laser reflectance interferometry to determine growth rate and stop growth at the desired thickness. Gas composition, which consisted of varying amounts of H₂, Ar and CH₄ or C₆₀, gas pressure, microwave power, substrate temperature, growth rate, film thickness, rms surface roughness, friction coefficient and average ball wear rate for each film are contained in Table 1. Films A

through E were grown to comparable thickness to allow direct comparisons. Film F was grown to examine properties of thick films grown under these conditions. Film G was grown under typical $\text{H}_2\text{-CH}_4$ diamond growth conditions. A bare silicon substrate was also tested for comparison.

To introduce C_{60} into the reactor a quartz transpirator, shown in Figure 1, was attached. Fullerene rich soot, consisting of approximately 10% C_{60} , was purchased from MER corporation and placed in the transpirator. The soot was heated to 200°C under vacuum for 2 hours to remove residual gases and hydrocarbons. The tube furnace and transport tube were heated to between 550 and 600°C during operation to sublime C_{60} into the gas phase. Argon gas was passed through the transpirator to carry the C_{60} vapor into the plasma. To ensure that C_{60} was transported into the chamber, a silicon wafer was placed in front of the transport tube while maintaining a 14 sccm argon flow. With the reactor pressure at 100 Torr and the transpirator at 600°C , a 1.7 mg brown film was deposited on the wafer in one hour. The film displayed strong C_{60} infrared absorption features and no other features were observed. The measured Raman spectrum was also attributed to C_{60} . Based on these measurements, the transpirator is considered an effective source of C_{60} for diamond growth.

Films were also grown under similar low hydrogen content conditions using CH_4 instead of C_{60} as the carbon source. Exact comparisons are difficult because the amount of C_{60} introduced could not be precisely determined.

2.2 Film Characterization

The films were characterized by a variety of techniques, including Raman spectroscopy, x-ray diffraction measurements (XRD), Auger electron spectroscopy (AES), tunneling electron microscopy (TEM), atomic force microscopy (AFM), and scanning electron microscopy (SEM). Raman spectra of the films were measured with a Renishaw Raman microscope using a HeNe laser at 632.8 nm with an output power of 25 mW focused to a spot size of about $2\text{ }\mu\text{m}$. Raman spectroscopy is widely used to characterize

diamond films, although the small grain sizes in these films has a significant effect on the Raman spectrum. A Phillips powder diffractometer with Cu K_{α} was used for XRD measurements to ensure the presence of diamond and check for evidence of crystalline graphite. AES spectra were obtained using a physical electronics model 548 with double pass cylindrical mirror analyzer. The carbon KLL peak is sensitive to the bonding state of carbon, providing a qualitative means of assessing the sp^2/sp^3 ratio of the films. TEM imaging was performed in the JEOL 4000EXII operating at 400 kV. Specimens for TEM were prepared using standard dimpling and ion milling procedures. The surface was characterized using a Burleigh ARIS-3300 AFM to measure the rms surface roughness and a JEOL JXA-840A SEM to image the surface.

2.3 Friction & Wear Measurements

Friction and wear tests were performed with pairs of silicon nitride balls and diamond-coated silicon substrates on a ball-on-disk tribometer. Tests were run in dry nitrogen environments. A Plexiglas cover was fitted over the tribometer, permitting ultra dry environments to be created. A few pairs without the diamond films were also tested, primarily to assess and compare their tribological performance to those of pairs with a diamond film. The dead weight applied to the balls was 2 N. Frictional force was monitored with the aid of a linear variable-displacement-transducer and was recorded on a floppy disk via a data acquisition system throughout the tests. The rotational velocity was kept between 50 to 150 r/min. to provide sliding velocities of 25 to 40 mm/s. Sliding distance was 200 m. Wear-volume measurements on the balls were based on microscopic determination of the diameter of the circular wear scars. The wear of disk specimens was estimated from the traces of surface profiles across the wear tracks. Duplicate tests were run under conditions described above to check the reproducibility of the friction and wear data.

3. Results & Discussion

3.1 Characterization of Films

The films grown are characterized as nanocrystalline diamond films. Figure 2 shows XRD patterns from Films B-F. The characteristic (111), (220) and (311) diamond peaks are evident. The strong Si (400) peak due to the silicon substrate has been removed. There is no evidence of the strong (002) graphite peak at 26.4° . This indicates that the films contain diamond and no appreciable amounts of other crystalline material.

Evidence of low sp^2/sp^3 carbon ratios in the films is obtained from AES measurements of the carbon KLL peak shown in Figure 3. The KLL peak is sensitive to the bonding state of the carbon atom and has been used to determine sp^2/sp^3 ratios in a-C:H films.¹³ The AES spectra for Films C-F are very similar to that reported in the literature for diamond,^{14,15,16} indicating a low sp^2/sp^3 ratio. The AES spectrum of Film B appears to be somewhere between diamond and graphite, indicating a higher sp^2/sp^3 carbon ratio in this film.

High resolution TEM has been used to examine the microstructure of films grown with fullerene precursors and indicates the films are composed of small diamond grains (20 nm - 300 nm) with relatively clean grain boundaries.¹⁷ Figure 4 shows a HRTEM image of a section of Film A. The silicon substrate has been removed and a layer of gold deposited on the diamond. A 100 Å thick layer composed of amorphous carbon and diamond was immediately above the silicon substrate and formed preceding diamond film growth. The diamond grains are clearly visible above the amorphous layer and appear as well ordered diamond crystals. The boundaries between the grains are sharp and appear to contain little or no nondiamond phases. This further indicates these films are composed of nanocrystalline diamond films with little sp^2 carbon present.

Raman spectra of Films A-C and G are shown in Figure 5 which are representative of all the films grown. Raman spectra of Films E and F are similar to Film C while the Raman spectrum of Film D is similar to Film B. The Raman spectra show a peak at 1332 cm^{-1} attributed to diamond. Features at 1580 and 1330 cm^{-1} have been attributed to sp^2 carbon.¹⁸ An additional feature around 1140 cm^{-1} appears for Films A and C which has

been attributed to nanocrystalline diamond.^{19,20} For Film C, an intense fluorescence peak at 2250 cm^{-1} (1.68 eV) results in the rapidly rising background. The weak 1332 cm^{-1} peak relative to other Raman features for films grown at low hydrogen contents (Films A and C) is attributed to the small grain size in the films rather than an increase in the sp^2/sp^3 carbon ratio. The 1332 cm^{-1} peak intensity has been shown to decrease with decreasing grain size for both diamond films, where the grain size was determined from XRD measurements,²⁰ and for diamond particles of known size.^{21,22} Furthermore, these Raman spectra were excited using 632.8 nm light, which is more sensitive to the nondiamond carbon phases than the 488 nm Argon ion laser light commonly employed for measuring Raman spectra.²³ The present interpretation is supported by the TEM images, which indicate that Film A is nanocrystalline, as well as the AES and XRD data, which indicate the sp^2/sp^3 ratios of the films are similar to diamond and the only crystalline component in the films are diamond.

AFM measurements of rms surface roughness for Films A-E and G, all grown to $\approx 2\text{ }\mu\text{m}$, shows that higher carbon to hydrogen ratios lead to smooth film growth, while lower ratios lead to rougher films. Film F demonstrates that in these low hydrogen content plasmas, a $10\text{ }\mu\text{m}$ thick, smooth (rms roughnesses of 45 nm) film can be grown.

Figure 6A is a cross-sectional SEM micrograph of Film A. As is clear, the surface of this nanocrystalline diamond Film is rather smooth. Figure 6B shows that the wear track formed on Film A during tribological testing becomes extremely smooth.

3.2 Friction & Wear Data

As is evident from Figure 7, Film D with a rough surface finish exhibits a significantly higher friction coefficient than the smooth Film C in dry N_2 . As a reference, the friction coefficient of the Si substrate against the Si_3N_4 ball is also included in this Figure. The initial friction coefficient of rough diamond film is particularly high, i.e., ≈ 0.65 . Furthermore, the friction trace of this film is rather unstable and fluctuates between

0.15 and 0.27 at steady-state (see Figure 7). Table 1 shows the overall frictional performance and ball wear rate for both the rough and smooth diamond films. Again, the highest friction coefficients are due to rough diamond films, whereas the smooth diamond films exhibit friction coefficients of 0.04 to 0.08. We believe that the large fluctuations in the friction traces and very high initial friction coefficients of rough diamond films are largely due to ploughing and interlocking of asperities across the sliding interface. Sharp asperity tips of diamond crystals can dig in and cut the surface of softer counterface material, thus causing severe abrasion and ploughing. It is known that a high degree of ploughing can cause high frictional traction between sliding surfaces. This in turn promotes high friction and severe abrasion of the much softer counterface material. During successive sliding passes, the sharp asperity tips are progressively rounded and eventually blunted to result in a much smoother surface finish. Furthermore, the valleys between asperities are filled with a blanket of wear debris particles. The combination of these two physical phenomena produces a relatively smooth surface finish and eventually results in somewhat lower friction coefficients, i.e., 0.2 on rough diamond films as shown in Figure 7. This observation is consistent with the results of previous investigators who also reported very high friction coefficients for rough diamond films. In general, they found that the greater the surface roughness the higher the initial and steady-state friction coefficients for diamond films.⁴⁻¹⁰

Owing to their much smoother surface finish, Films A and C exhibit very low friction coefficients, i.e., 0.04 to 0.05, especially at steady-states (see Figure 7). These values are comparable to that of a natural diamond in dry N₂ as reported in Ref. 8. As shown in Figure 6a, the surface asperities of these films are not faceted and sharp. Most importantly, the sliding contact surfaces of these films become exceedingly smooth under the influence of repeated sliding (see Figure 6b). As a result, the extent of frictional losses during sliding against Si₃N₄ remain low, especially after a break-in regime of the sliding

tests. In short, these films cause much lower ploughing, hence very little fluctuation in friction traces during sliding.

Table 1 lists the wear rates of Si_3N_4 balls during sliding against various diamond films. As is evident, compared to smooth diamond films, rough diamond films cause much higher wear losses on counterface balls. This can be attributed to severe abrasion caused by the sharp asperity tips and edges of rough diamond crystals, whereas the smooth films result in much lower wear losses on the Si_3N_4 ball.

4. Conclusions

Nanocrystalline diamond films have been deposited using a microwave plasma consisting of argon, 2-10% hydrogen and a carbon precursor such as C_{60} or CH_4 . It is possible to grow the diamond phase with both C_{60} or CH_4 , although the hydrogen concentration in the plasma was 1-2 orders of magnitude lower than normally required in the absence of the argon. The Ar-grown films have been shown to be nanocrystalline diamond films which grow with a relatively smooth surface. In fact, 10 μm thick films (Film F, Table 1) with rms surface roughnesses of 45 nm have been grown under low hydrogen content conditions. Pin-on-disk friction measurements indicate that the smooth Ar-grown films have friction coefficients of 0.04-0.06, 2-3 times lower than the H_2 - CH_4 grown rough diamond films of comparable thickness.

Acknowledgments

The authors would like to acknowledge the Electron Microscopy Center for Materials Research at Argonne National Laboratory, where the TEM analysis was performed. We would also like to thank Dr. Ben Tani for the x-ray diffraction results. This work was supported by the U.S. Department of Energy, BES-Materials Sciences, under contract W-31-109-ENG-38.

Table 1. The growth conditions, average growth rate, film thickness, surface roughness, friction coefficient and ball wear rate for each film is listed.

Figure 1. Schematic diagram of the fullerene transpiration source.

Figure 2. XRD measurements for Films B-F showing diamond is the only crystalline material present in the films. The (400) peak from the silicon substrate has been removed for clarity.

Figure 3. The AES spectra for Film B and Films D-F are very similar to diamond. Film C appears to be between diamond and graphite, indicating a higher sp^2/sp^3 carbon ratio in this film.

Figure 4. HRTEM image of Film A. The silicon substrate has been removed and a gold layer deposited on top. An amorphous carbon layer was formed on top of the silicon before diamond growth began. The diamond grain boundaries are sharp, with little evidence of sp^2 carbon.

Figure 5. Raman spectra show a diamond peak at 1332 cm^{-1} as well as features at 1580 and 1320 cm^{-1} which are attributed to sp^2 carbon. Films A and C show an additional feature at 1140 cm^{-1} which has been attributed to nanocrystalline diamond.

Figure 6. SEM micrographs of Film A (A) before tribological testing and (B) the wear track after tribological testing.

Figure 7. Variation of the friction coefficients of Films C, D and an uncoated silicon substrate during sliding against Si_3N_4 balls in dry N_2 under a 2 N load.

-
- ¹C.P. Klages, Appl. Phys. A 56, 513 (1993).
- ²W. Zhu, B.R. Stoner, B.E. Williams, and J.T. Glass, Proc. IEEE 79, 621 (1991).
- ³W.A. Yarbrough and R. Messier, Science 24, 688 (1990).
- ⁴S. Jahanmir, D.E. Deckman, L.K. Ives, A. Feldman and E. Farrabaugh, Wear 133, 73 (1989).
- ⁵A.K. Gangopadhyay and M.A. Tamor, Wear 169, 221 (1993).
- ⁶P.J. Blau, C.S. Yust, L.J. Heatherly, and R.E. Clausing, Proc. Leeds-Lyon Conf., (D. Dowson, C.M. Taylor, and M. Godet, eds.), Leeds-Lyon Tribology Series, Elsevier Science Publishers, Amsterdam, Vol. 17., p. 399, 1990.
- ⁷S.S. Perry, J.W. Ager, G.A. Somorjai, J. Mater. Res. 8, 2577 (1993).
- ⁸B.K. Gupta, A. Malshe, B. Bhushan and V.V. Subramaniam, J. Tribology 116, 445 (1994).
- ⁹I.P. Hayward, I.L. Singer and L.E. Seitzman, Wear 157, 215 (1992).
- ¹⁰M. Kohzaki, K. Higuchi, S. Noda and K. Uchida, J. Mater. Res. 7, 1769 (1992).
- ¹¹D.M. Gruen, S. Liu, A.R. Krauss, and X. Pan, J. Appl. Phys. 75, 1758 (1994).
- ¹²D.M. Gruen, S. Liu, A.R. Krauss, J. Luo, and X. Pan, Appl. Phys. Lett. 64, 1502 (1994).
- ¹³A. Fuchs, J. Scherer, K. Jung and H. Ehrhardt, Thin Solid Films, 232, 51 (1993).
- ¹⁴S. Craig, G.L. Harding and R. Payling, Surf. Sci. 124, 591 (1983).
- ¹⁵S. Kasi, H. Kang, J.W. Rabalais, Phys. Rev. Lett. 59, 75 (1987).
- ¹⁶A. Badzian and T. Badzian, Appl. Phys. Lett. 62, 3432 (1993).
- ¹⁷J.S. Luo, R. Csencsits, D.M. Gruen, A.R. Krauss, X.Z. Pan, and S.Z. Liu, (Manuscript in preparation).
- ¹⁸D.S. Knight and W.B. White, J. Mater. Res. 4, 385 (1989).
- ¹⁹R.J. Nemanich, J.T. Glass, G. Lucovsky, and R.E. Shroder, J. Vac. Sci. Technol. A 6, 1783 (1988).
- ²⁰W.A. Yarbrough and R. Roy, Proc. Mat. Res. Soc. EA-15, 33 (1988).
- ²¹Y. Namba, E. Heidarpour and M. Nakayama, J. Appl. Phys. 72, 1748 (1992).
- ²²M. Yoshikawa, Y. Mori, M. Margawa, G. Katagiri, H. Ishida, and A. Ishitani, Appl. Phys. Lett. 62, 3114 (1993).
- ²³J. Wagner, C. Wild, and P. Koidl, Appl. Phys. Lett. 59, 779 (1991).

Film	Sample ID #	H ₂ Flow	Ar Flow	CH ₄ Flow	C ₆₀ T-furn	Pres.	Power	Substr Temp	Growth Rate	Diamond Thickness	RMS Roughness	Friction Coef.	Wear Rate x10 ⁻⁶
		sccm	sccm	sccm	°C	Torr	W	°C	µm/hr	µm	nm		mm ³ /Nm
A	940825	2	100	0	600	100	1500	850	0.3	1.7	30	0.05	0.2
B	940926B	10	90	0	630	100	1500	850	0.9	2.0	105	0.18	0.15
C	940927	2	98	0	630	100	1500	850	0.25	2.0	41	0.04	0.1
D	940928	10	90	0.8	20	100	1500	850	0.8	2.0	125	0.21	0.88
E	940929	1.5	98	0.8	20	100	1500	850	0.5	2.3	53	0.08	0.4
F	941013	2	100	1	20	100	800	850	0.7	10	45	-	-
G	950112A	98	0	2	20	60	1500	850	0.4	2.0	95	0.12	0.48
	Silicon	-	-	-	-	-	-	-	-	0	<3	0.42	1.2

Table 1

Figure 1.

Figure 2.

Figure 3.

a-C+ diamond (no Si)

Figure 5.

Figure 6A.

Figure 6B.

Figure 7.