Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Presented at the Materials Research Society Conference, Boston, MA, November 27–December 2, 1989, and to be published in the Proceedings

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November 1989

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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LBL-28348

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This work was supported by the National Science Foundation through Grant MSE-8800149 with the University of California at Berkeley, by the Computer Mechanics Laboratory at University of California at Berkeley, and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

POWER DENSITY EFFECTS IN THE PHYSICAL AND CHEMICAL PROPERTIES OF SPUTTERED DIAMOND-LIKE CARBON THIN FILMS

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ABSTRACT

Thin films of diamond-like amorphous carbon were prepared by dc magnetron sputtering. A systematic variation in the physical properties of the films (mass density and electrical resistivity) was found as a function of sputtering power density. Chemical bonding and microstructure of the carbon thin films were investigated using electron energy loss spectroscopy (EELS) and Raman spectroscopy. Films grown at a lower power density were found to have more sp^3-bonded atomic sites and larger graphite microcrystals than films produced at higher sputtering power densities.

INTRODUCTION

Diamond-like amorphous carbon thin films have attracted much attention due to their useful and unique properties, e.g., high hardness, high electrical resistance, optical transparency in the infrared region, and chemical inertness. These films have been used as hard overcoats for magnetic storage media and as optical coatings, and in various other applications for wear and corrosion protection. Such carbon films are produced by a variety of techniques, such as hydrocarbon plasma-assisted chemical vapor deposition, ion-beam sputtering deposition, and magnetron sputtering techniques [1-4]. The macroscopic properties of the films have been reported to vary depending on the deposition method and conditions [5].

Carbon has two allotropic crystalline states, graphite and diamond, composed of sp^2 and sp^3 hybrid covalent bondings, respectively. The unique macroscopic properties of diamond-like amorphous carbon films may result from the microstructure and chemical bonding of the carbon atoms. The ratio of sp^2 to sp^3 chemical bondings has been regarded as a key issue in understanding the behavior of diamond-like carbon films. In order to identify chemical bonding distributions, electronic band structures and phonon density of states of solid film have been investigated using the interaction of lasers, incident accelerated electrons, and X-rays with solid carbon thin films [6-9].

In this study, the effect of sputtering power density has been investigated by growing diamond-like amorphous carbon films under well-controlled conditions. The main focus is on determining the microstructural differences between the carbon thin films prepared at different sputtering power densities and relating the differences to their properties.

EXPERIMENTAL

Sample preparation

Magnetron sputtering was used to produce diamond-like amorphous carbon thin films. A graphite target with a diameter of 3.0 inches was used as the carbon source. Pure Ar gas was introduced into the chamber and ionized by use of dc power. Total pressure was kept at 10 mTorr.

Samples were produced with sputtering power densities of 0.1, 1.1, 2.1, and 10 watts/cm^2. No substrate bias voltage was applied; no heat was supplied to the substrates from outside.

NaCl and Si were used as substrates. Carbon films with thicknesses of 300-400 Å deposited on NaCl were used for TEM and Raman spectroscopy studies. For the TEM studies, the films were separated from the NaCl substrates by dissolving the NaCl in distilled water. For mass density determinations, carbon films with thicknesses of about 1 μm were produced on Si substrates; the Si substrates were etched with HF acid in order to avoid delamination due to severe stress in these thick films.

Characterization techniques

Electron energy loss spectra were obtained using a JEOL 200 CX electron microscope operating at 200 kV. A parallel electron energy loss spectrometer (Gatan 666) with a resolution of 1.2 eV was used to analyze the energy distribution of electrons transmitted through the specimen .

Raman spectra were obtained between 1000-2000 cm^{-1} using the 488 nm Ar^+ laser line. The Raman spectra were fit using the sum of two Gaussian line shapes and a linear background.

Measurement of physical properties

The mass density of each film was determined by measuring its weight and volume. Film thickness was measured with a profilometer. The net weight of each film was determined from the difference between the weight of the substrate prior to deposition of the film, and the weight of the substrate and film after deposition. The error range of the balance was 10^{-5} g. A four-point probe apparatus was used to measure the electrical resistivity of the films.

RESULTS AND DISCUSSION

Electron energy loss spectroscopy

Electron energy loss spectra were collected from graphite and the thin carbon films. An example of the low-loss region of each spectrum is illustrated in Fig. 1. Spectra a, b, c, and d in Fig. 1 were obtained from graphite and samples prepared at 10, 2.1, and 0.1 watts/cm^2, respectively; these samples are referred to as samples A, B, C, and D in this paper. Two prominent peaks are seen at 6.4 eV and 27 eV in spectrum a. The losses associated with features in this energy range are normally related to either plasmon oscillations or interband transitions of valence electrons [10]. In particular for graphite, it is known that the peak at 6.4 eV corresponds to plasmon oscillations of the π electrons in the valence band,

and the peak at 27 eV arises from the collective excitation of all the valence electrons ($\pi + \sigma$) [11,12].

The plasmon resonances of diamond-like carbon films appear at a lower energy value than those of graphite, as shown in Fig. 1. Strong π plasmon oscillations are observed at 6.0 eV, 6.0 eV, and 5.0 eV for samples B, C, and D, respectively, while the $\pi + \sigma$ peaks are found at nearly the same energy, 24.5 eV.

Using a simple free electron gas model, one can establish a quadratic relationship between valence electron density and plasmon frequency [13]. Hence, samples B, C, and D appear to have nearly the same total density of $\pi + \sigma$ electrons, but the density of π electrons for samples B and C is higher than that of sample D. These results indicate that more sp^2-bonded atomic sites are present in samples B and C than in sample D, while the sp^3/sp^2 ratio in sample B is similar to that in sample C.

Raman spectrometry

Raman spectra were obtained from samples A, B, C, and D. Fig. 2 shows spectra obtained from samples B and D for comparison. Each plot consists of the experimental data and the fitted curves. The "G" line positions for samples B and D are seen at 1558 cm^{-1} and 1541 cm^{-1} respectively, while the "D" line positions are observed at 1379 cm^{-1} and 1368 cm^{-1}, respectively. The integrated intensity ratio I_d/I_g for sample D is lower than that of sample B.

Raman spectra for the two crystalline forms of carbon are very well known; the first-order Raman spectra of highly ordered pyrolitic graphite and of diamond have peaks at 1580 cm^{-1} and 1332 cm^{-1}, respectively. A peak in the graphite spectrum near 1350 cm^{-1} appears in disordered graphite [6,14]. This

peak increases in intensity relative to the intensity of the 1580 cm^{-1} peak as the microcrystallite size, L_a, decreases [15]. Raman spectra of amorphous solids feature broad bands related to the phonon density of states [16]. In particular, for amorphous carbon, the positions of the "G" and "D" peaks shift and the linewidth increase from those of graphite as disorder and the fraction of sp^3-bonded atomic sites increases [17,18]. Therefore, the band positions may yield information about bond-angle disorder and bonding in the amorphous carbon films.

The "G" band position of sample D in Fig. 2b is shifted to a lower frequency by about 17 cm^{-1} compared to that of sample B, which in turn is shifted by 22 cm^{-2} from the frequency in graphite. The shift may indicate that sample D has a higher concentration of sp^3-bonded atomic sites than sample B. A calculation by Richter et al. using a mixture of sp^2- and sp^3-bonded atomic sites and C-C force constants yields shifts in the "G" line frequency for sp^3-bonded fractions of 15% and 5%, which are similar to those observed in samples D and B, respectively.

If the linear relationship between I_d/I_g and $1/L_a$ continues beyond the experimentally observed region, then the ratios of I_d/I_g for samples B and D indicate that the size of graphite microcrystallites decreases as the sputtering power density increases. These interpretations of the data suggest that the total volume of sp^3-bonded atomic sites in sample R is higher than in sample P.

Physical properties

Fig. 3 shows the electrical resistivity of carbon thin films grown at various sputtering power densities. A rapid decrease in electrical resistivity is observed

as the power density increases below 2.1 watts/cm^2. As was discussed in the EELS and Raman spectroscopy sections, samples deposited at the relatively higher power densities have higher percentages of sp^2-bonded atomic sites. The increase in sp^2-bonded atomic sites and higher density of π electrons near the Fermi energy level is believed to result in lower electrical resistivity.

The mass density of carbon thin films is also shown in Fig. 3. Increasing the sputtering power density from 0.1 to 10 watts/cm^2 results in a decrease in film density, from 2.1 to 1.75 g/cm^3. The mass density of samples appears to vary from that of pyrolitic graphite (1.6-1.95 g/cm^3) to that of single crystal graphite (2.26 g/cm^3). The mass density of sample D is close to that of crystalline graphite; however, the results of EELS and Raman spectroscopy studies show that sample D is amorphous. The relatively high mass density results from the particular arrangements and/or distributions of the sp^3- and sp^2-bonded atomic sites, and is not due to the enlargement or growth of graphite microcrystals.

CONCLUSION

EELS and Raman spectroscopy were used to determine the microstructural variation of carbon thin films depending on deposition conditions. It has been shown that the chemical bonding distributions and microstructure of diamond-like carbon thin films are affected by sputtering power density. Films produced at a lower sputtering power density have more sp^3-bonded atomic sites and larger graphite microcrystals than films grown at higher sputtering power densities. The electrical resistivity in diamond-like carbon films is consistent with a microstructure containing both sp^2- and sp^3-bonded carbon. As the fraction of sp^2-bonded atomic sites increases, the higher probability for orbital

overlap and the higher density of π electrons results in the reduction of electrical resistivity. More efforts are being made to determine such physical properties as hardness, optical band gap, and residual stress in order to obtain a better understanding of the relationship between the microstructure and the physical properties of the films.

ACKNOWLEDGMENTS

The authors would like to thank Mr. C.J. Echer for assistance in using the microscope facilities at the National Center for Electron Microscopy. This work was supported by the National Science Foundation through Grant MSE-8800149 with the University of California at Berkeley, by the Computer Mechanics Lab. at UCB, and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098

REFERENCES

1. D.A. Anderson, Phil. Mag., 35, 17, (1977).

2. A. Bubenzer, B. Dischler, B. Brandt, and P. Koidl, J. Appl. Phys., 54(8), 4590, (1983).

3. C. Weissmantel, K. Bewilogua, K. Breuer, D. Dietrich, U. Ebersbach, H.J. Erler, B. Rau and G. Riessen, Thin Solid Films, 96, 31, (1982).

4. N. Savvides, J. Appl. Phys., 58, 518, (1985).

5. H. Tsai and D.B. Bogy, J. Vac. Sci. Tech., A5(6), 3287, (1987).

6. R.O. Dillon, J.A. Woollam, and V. Katkanant, Phys. Rev.B, 29(6), 3482, (1984).

7. N. Wada, P.J. Gaczi, and S.A. Solin, J. Non-Cryst. Solids, 35, 543, (1980).

8. F.R. McFeely, S.P. Lowlaczyk, L. Ley, R.G. Cavell, R.A. Pollak, and D.A. Shirley, Phys. Rev., B9, 5268, (1974).

9. P.E. Batson and A.J. Craven, Phys. Rev. Lett., 42, 893, (1979).

10. H. Raether, in Excitation of Plasmons and Interband Transitions by Electrons, Springer-Verlag.

11. W.Y. Liang and S. Cundy, Phil. Mag., 19, 1031, (1969).

12. E.A. Taft and H.R. Phillip, Phys. Rev., 138, 197, (1965).

13. D.B. Williams and J.W. Edington, J. Microscopy, 108(2), 113, (1976).

14. R.J. Nemanich and S.A. Solin, Phys. Rev.B, 20(2), 392, (1979).

15. F. Tuninstra and J.L. Koenig, J. Compos. Mater., 4, 492, (1970).

16. R. Zallen, in The Physics of Amorphous Solids, (Wiley-Interscience Pub., NY, 1983).

17. D. Beeman, J. Silverman, R. Lynds, and M.R. Anderson, Phys. Rev.B, 30, 870, (1984).

18. A. Richter, H.-J. Scheibe, W. Pompe, K.-W. Brzezinka, and I. Muhling, J. Non-Cryst. Solids, 88, 131, (1986).

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FIGURE CAPTIONS

Fig. 1. Electron energy loss spectra in the plasmon region: (a) sample A (graphite); (b) sample B, prepared at 10.0 watts/cm^2; (c) sample C, prepared at 2.1 watts/cm^2; (d) sample D, prepared at 0.1 watts/cm^2.

Fig. 2. Raman spectra of the diamond-like carbon films. Spectra for sample B, prepared at 10.0 watts/cm^2, and sample D, prepared at 0.1 watts/cm^2, are shown in (a) and (b), respectively. The experimental data and fit are illustrated.

Fig. 3. Electrical resistivity and mass density of the diamond-like carbon films vs sputtering power density.

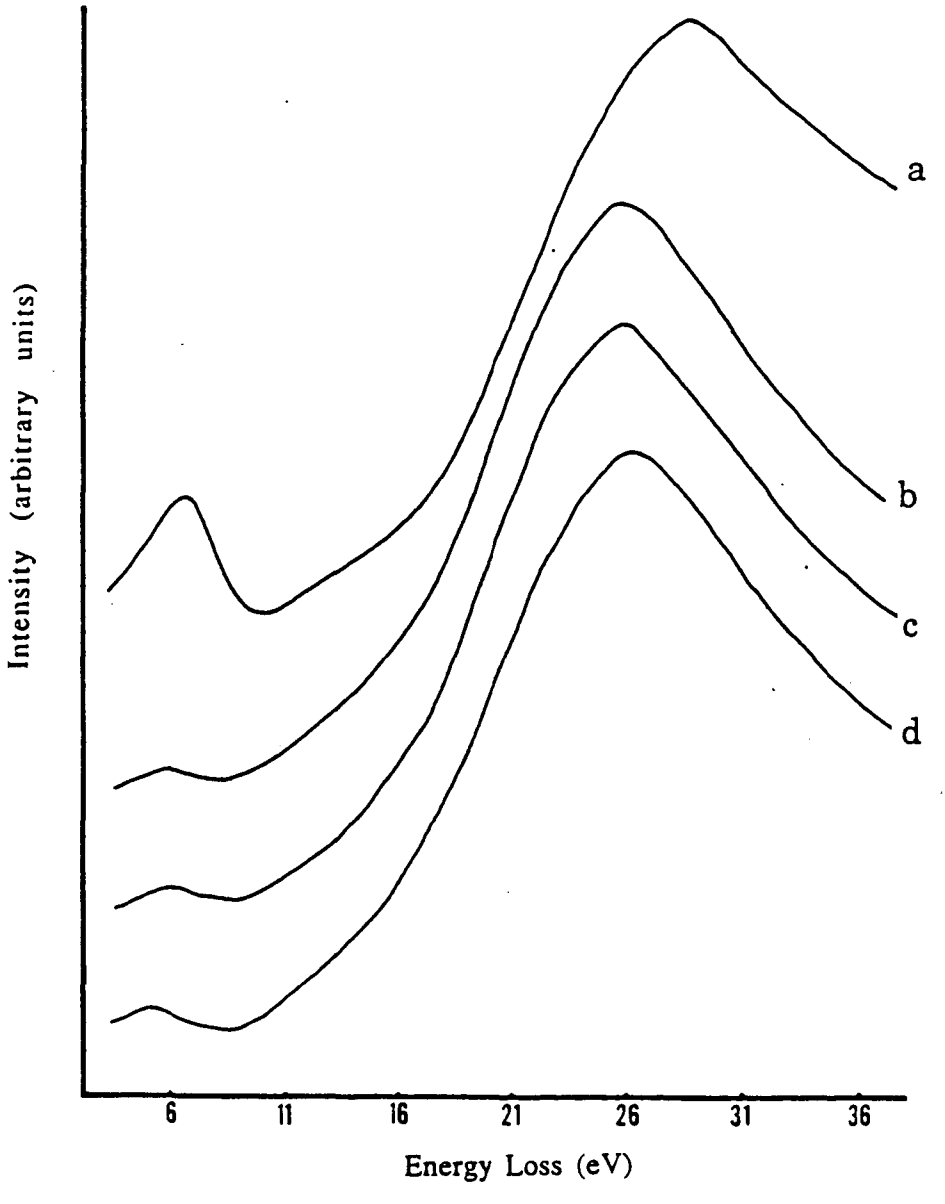
Intensity (arbitrary units)
a
b
c
d
6
11
16
21
26
31
36
Energy Loss (eV)

Fig. 1

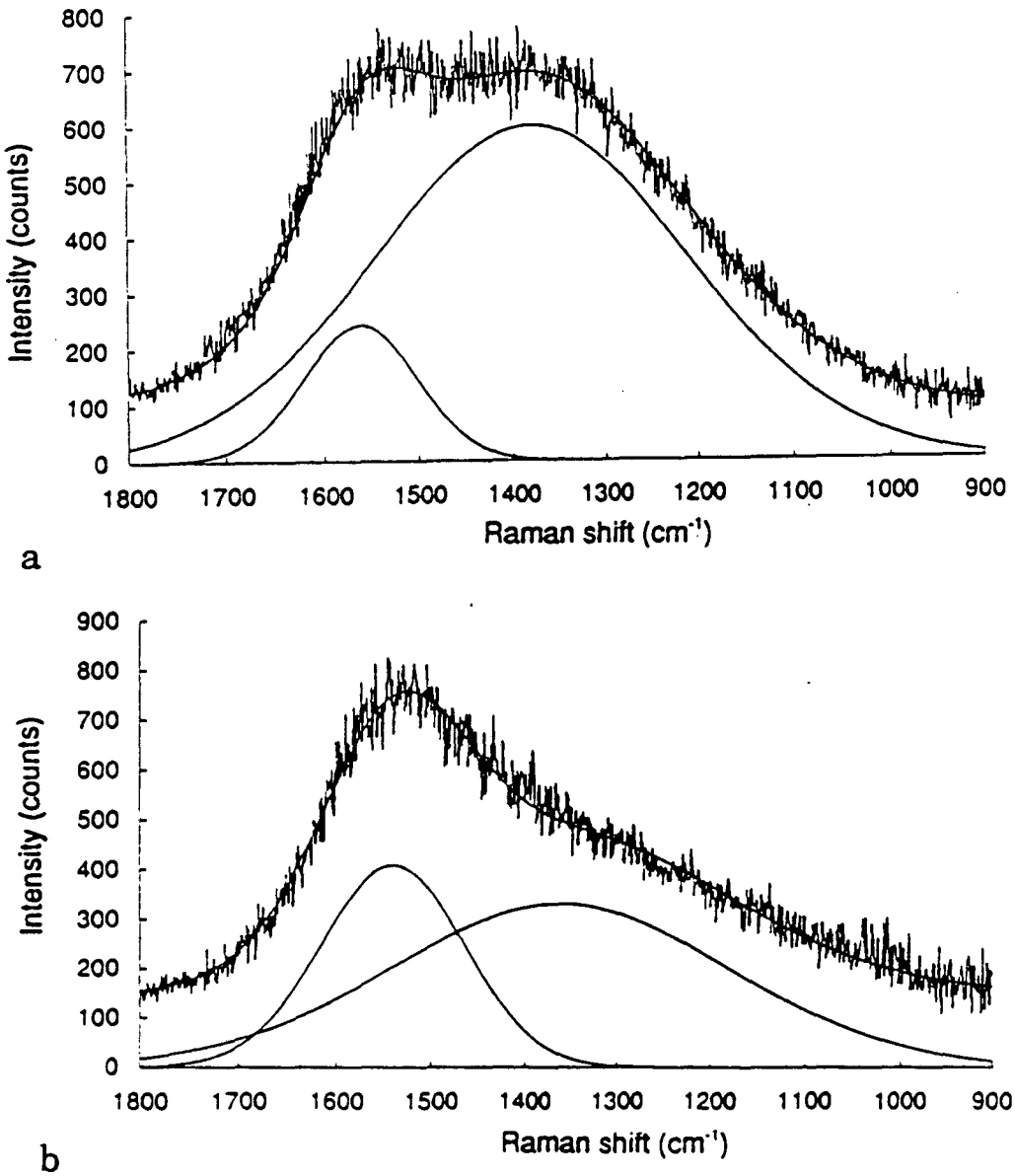
800
700
600
500
400
300
200
100
0
Intensity (counts)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
Raman shift (cm-1)
a
900
800
700
600
500
400
300
200
100
0
Intensity (counts)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
Raman shift (cm-1)
b

Fig. 2

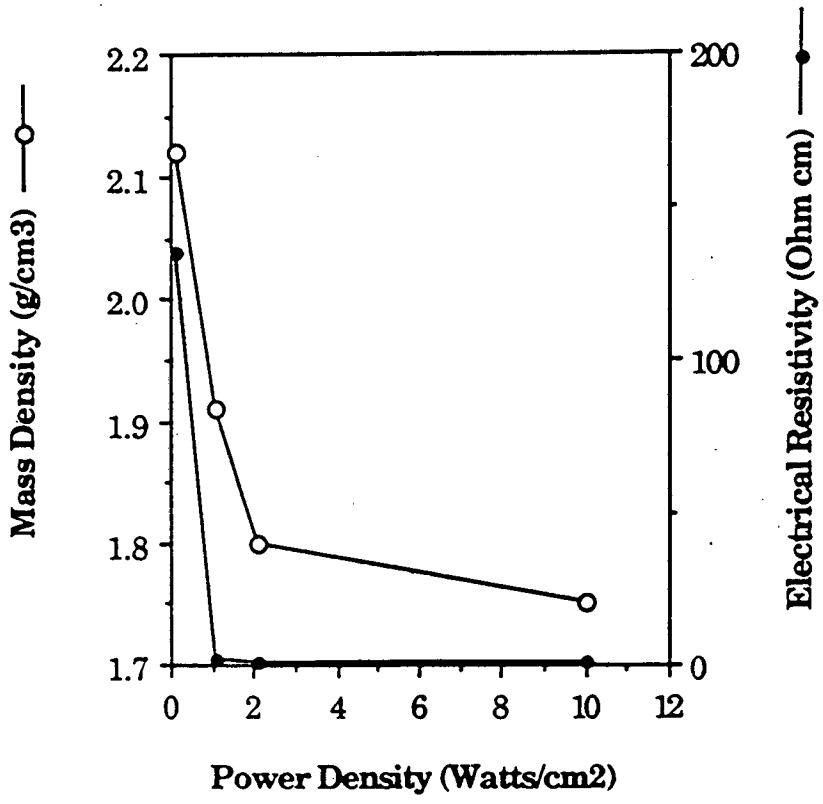
Mass Density (g/cm3)
Electrical Resistivity (Ohm cm)
Power Density (Watts/cm2)
2.2
2.1
2.0
1.9
1.8
1.7
200
100
0
0
2
4
6
8
10
12

Fig. 3

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