

Optical and Mechanical Properties of D.C. Sputtered Carbon Films

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Abstract

Amorphous carbon films were deposited on glass by d.c. magnetron sputtering from a graphite target in mixtures of argon and hydrogen. Hydrogen flow and other deposition parameters affected the optical and mechanical properties of these films. Increasing hydrogen content caused the average visible transmittance to vary from 16% to 86% for 500-Å thick films. Maximum compressive stress and hardness occur between 0-1% hydrogen flow, resulting in rapid delamination. Low sputtering power moderately increases transmittance and hardness while relieving stress. Transparency is induced in both the high-hydrogen and low-power films by formation of sp^3 C-C bonds. In the case of the hydrogenated films, however, a softer polymeric structure is formed.

Introduction

This paper describes the effect of hydrogen content and sputtering power on the optical and mechanical properties of sputtered carbon films. Films having properties resembling those of diamond would have numerous applications as protective optical coatings. Carbon coatings have been used to antireflect and protect semiconductor optics in the midinfrared¹⁻⁴ where the coatings are highly transparent. Visible and near infrared transmittance of carbon films can also be enhanced by suitable choice of deposition parameters. High visible transmittance alone is not a sufficient criterion for a viable coating. The hardness of diamond as well as good adhesion of the film must also be realized for carbon coatings to have value for optical applications.

Amorphous hydrogenated carbon films, designated a-C:H, can have a wide range of properties falling between those of graphite and diamond, as illustrated in a recent review.⁵ Near the latter extreme, the films may be referred to as "diamond like". Diamond-like films are often produced by glow-discharge decomposition of methane or other hydrocarbon gases. Diamond-like films have also been produced by direct ion-beam deposition of carbon and by sputtering. Films produced by these methods need not contain hydrogen and can be simply designated as a-C. Reactive d.c. magnetron sputtering at low temperatures, as used in this study, can produce either a-C:H or simply a-C.

In the next section, we describe the sputtering process used to deposit a-C:H films and the optical and mechanical techniques used to characterize them. Then we present the optical transmittance, intrinsic stress, and hardness as a function of such parameters as hydrogen flow rate and sputtering power. We will show that under some conditions the films will become more diamond-like, but not necessarily in both electronic and mechanical properties.

Film Growth and Characterization

The films described herein were deposited by reactive dc magnetron sputtering. The target was a 99.99%-pure graphite disk, 75 mm in diameter, bonded to a water-cooled copper backing plate. The substrates were located 4 cm below the target on a heated stainless-steel platform. The sputtering atmosphere was a mixture of argon and hydrogen. Total pressures ranged from 5-50 mTorr with the H₂ flow ranging from 0-20 %. The discharge could be sustained with powers as low as 5 W to a maximum of about 500 W. During deposition, the unheated substrate temperatures rose to a value between 26 °C and 89 °C, depending on the power. In some depositions, the substrate temperature was deliberately raised to between 100-500 °C.

Deposition rates were measured during deposition with a quartz crystal monitor calibrated by external measurements on a stylus profilometer. The deposition rate increases linearly with power to about 5 Å/s at 500 W and a total pressure of 10 mTorr. These rates are comparable to those typically obtained using glow-discharge decomposition (1-3 Å/s). Compared to the sputtering rates of most metals and even oxides these rates are low. Increasing the flow rate of H₂ has little effect on deposition rate. A sudden drop in rate accompanying a transition to a compound target is frequently observed in reactive sputtering with O₂ or N₂, but is not seen in this process.

Fourier-transform infrared (FTIR) spectroscopy was used to determine the actual hydrogen content of the films. Infrared-transparent NaCl substrates were coated with films 1.0- μm thick. The amount of bound hydrogen is believed to be proportional to the integrated intensity of a cluster of C-H stretch bands centered around 2900 cm⁻¹.^{2,6-9}

Optical transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were measured over near-ultraviolet, visible and near-infrared wavelengths ($\lambda=180-2500$ nm). Silica plates and glass microscope slides were used as substrates. Spectral properties were averaged over the visible spectrum weighted by the photopic response of the eye, and over the solar spectrum weighted by the solar spectral irradiance. The optical constants were determined by numerical solution to the equations for R and T . The extinction coefficient was then used in finding the optical band gap by means of a Tauc plot.

Film stress was determined by using a surface profilometer to measure the induced curvature of the substrates. We deposited films with thickness $t_f=180$ nm onto glass cover slips of thickness $t_s=0.15$ mm and masked length $l=22$ mm. According to Goranchev¹⁰ film stress is related to the deflection δ measured at the center of the strip by

$$\sigma = \frac{4E_s t_s^2 \delta}{3(1-\nu_s) l^2 t_f} ,$$

where Young's modulus $E_s=70.3$ GPa and Poisson's ratio $\nu_s=0.22$. Hardness of the films was measured using a displacement microindenter. For the hardness measurements, films were deposited to a thickness of 0.6-1.0 μm on Si wafers.

Film Properties

Visible transmittance of sputtered films was observed to increase when deposited in the presence of hydrogen gas.¹²⁻¹⁴ We have systematically varied the percentage flow of H_2 in order to examine the full range of hydrogen content. In contrast to sputtering in Ar, glow-discharge decomposition of hydrocarbons usually produces a-C:H films that are nearly saturated with hydrogen. Application of a bias voltage to the substrate, however, causes ion bombardment of the growing film and preferentially removes hydrogen from the surface. In this process, the transmittance and band gap

have been observed to decrease with bias.^{2,7,8,11}

Among the various deposition parameters investigated, addition of H₂ to the sputtering gas had the most pronounced effect on the optical transmittance. Fig. 1 gives the spectral transmittance for a series of 500-Å-thick films deposited at 10 mTorr total pressure and 200 W input power for several H₂ flow rates. A flow rate of even 1% H₂ greatly increases the transmittance over films made in pure argon. The broad absorption edge of the films made without hydrogen gives the films a brown appearance while the films made with higher levels of hydrogen appear faintly yellow. The optical band gap of these films increases from 0.45 to 2.12.

FTIR spectroscopy shows that the bound hydrogen content of the films approaches a limiting value when the H₂ flow rate reaches about 5%. In Fig. 1, this flow rate corresponds roughly to the limiting value of optical transmittance. Maximum hydrogen concentration in a-C:H films has been reported to fall between 30-50%¹⁴⁻¹⁸ using elastic recoil detection and nuclear reaction analysis. Hydrogen in excess of 30 % may be weakly bound and not observable by FTIR spectroscopy.⁷

The effect of hydrogen flow is shown in terms of averaged transmittance values in Fig. 2. For films made in pure argon the visible transmittance is 0.16, which is unacceptably low for most applications. At a H₂ flow rate of only a few percent, the transmittance of the film is nearly a maximum, reaching $T_v=0.86$ for 10% H₂. The reflectance of the films decreases as H₂ and transmittance increase. This is due to a decrease in the index of refraction, outweighing an increased contribution from the second surface caused by lower absorption in the film.

The transmittance can also be increased by decreasing the sputtering power pure Ar. Figure 3 shows the variation in average transmittance with power at 10 mTorr on unheated substrates. In this case the transmittance rises from 0.16 to less than 0.40.

Most of the increase occurs at the lowest power levels where deposition rates are very slow. No compositional changes are occurring in this case, but it has been proposed that an increasing fraction of the carbon bonds form with diamond-like sp_3 character.¹⁹

Substrate temperatures in the range of 60 to 400 °C have little effect on the optical transmittance of films made in pure Ar. The transmittance of films made with 10 % H_2 flow, however, drops from 0.86 to 0.75. This effect may simply be due to preferential reemission of hydrogen at elevated temperatures. This observation is in general agreement with results of annealing experiments on films made by CVD and ion beam deposition.^{6,20,24} The small change in optical properties over the low temperature range also indicates that the effect of power on optical properties as described above is not indirectly caused by the change in temperature with power.

Although diamond is known to be hard and chemically resistant, these attributes are useless if the film does not adhere to the substrate. The films made with H_2 flow between 0.5 and 1.0% delaminate very quickly, even when only a few hundred Angstroms thick. In pure Ar, and at H_2 flows greater than 1%, the films appear to be more adhesive. The tendency of some films to delaminate can be caused by intrinsic stress in the film, which is measured by substrate bending. Figure 4 shows that all of the films are in compressive stress. The maximum stress occurs between 0 and 1% H_2 flow but we cannot quantify the stress in this range because the films instantly delaminate upon exposure to air. At higher hydrogen concentrations the stress gradually diminishes.

The stress maximum in Fig. 4 is usually not seen in plasma deposited films which typically have high hydrogen content even with ion bombardment of the substrate. Enke,²¹ however, observed a turnover in stress for plasma deposited films at low pres-

sure and high bias voltage. This result adds to evidence that the plasma decomposition and sputtering processes produce similar films when a complementary set of parameters are chosen. Kerwin et al., on the other hand, measure stress in sputtered films and observe only the diminishing tail. Possibly they could not reach the low hydrogen regime because of suspected contamination from residual water vapor. Zelez,⁴ and Zou,⁸ however, deposited films with diminishing compressive stress becoming tensile at high bias voltages despite high pressures of hydrocarbon gas.

A generally decreasing trend was observed in the hardness of the films as hydrogen content increases. Figure 5 shows that the hardness decreases slightly going from 0% H₂ to 0.5% H₂ and then decreases sharply. These results are probably lower than the true values because of local delamination around the indentation point. This is especially likely for the 0.5% and 1.0% films where delamination is visually apparent, but may also be true to a lesser extent for the other films. Such an adjustment would bring the hardness profile into closer correlation with the stress profile of Fig. 4. Weissmantel et al.²² and Scharff²³ observed a downturn in hardness for high bias and low pressure of hydrocarbon gas and therefore presumably low hydrogen content in support of the above contention.

As power decreases, compressive stress slowly decreases while hardness slowly increases as shown in Figures 6 and 7. The rate of change becomes more rapid at very low power levels. This effect was previously observed with greater magnitude using a nonstandard sputtering technique in which an "unbalanced" magnetron produces a high ion flux at the substrate.¹⁹

Conclusion

Addition of H₂ during sputtering of carbon films increases H concentration and visible transmittance. Stress and possibly hardness, however, reach a peak well before the transmittance approaches its limiting value. Thus, the films are not simply becoming more like diamond with increasing H content. Hydrogen causes the character of the C-C bonds to shift from sp² to sp³ giving clearer films, but the rising number of C-H bonds ultimately relieves stress and produces a softer "polymer-like" material. Low power deposition, like the presence of hydrogen, appears to stabilize the formation of sp³ C-C bonds, increasing transparency and band gap. In this case, however, the high transmittance films not only have relieved stress and better adhesion, but also higher hardness. Unfortunately, low power also means impractically low deposition rates. Our preliminary results show that better optical and mechanical properties can be achieved at high power and rate with the use of concurrent ion bombardment.

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References

1. T.J. Moravec and J.C. Lee, *J. Vac. Sci. Technol.* **20** 338 (1982).
2. A. Bubenzer, B. Dischler, G. Brandt, and P. Koidl, *J. Appl. Phys.* **54** 4590 (1983).
3. M.J. Mirtich, D. Nir, D. Swec, and B. Banks, *J. Vac. Sci. Tech.* **A4** 2680 (1986).
4. J. Zelez, *RCA Rev.* **43** 664 (1982).
5. H. Tsai and D.B. Bogy, *J. Vac. Sci. Technol.* **A5** 3287 (1987).
6. B. Dischler, A. Bubenzer, and P. Koidl, *Solid State Comm.* **48** 105 (1983).
7. P. Couderc and Y. Catherine, *Thin Solid Films* **146** 93 (1987).
8. J.W. Zou, K. Reichelt, K. Schmidt, and B. Dischler, *J. Appl. Phys.* **65** 3914 (1989).
9. J. Gonzalez-Hernandez, B.S. Chao, and D.A. Pawlik, *J. Vac. Sci. Technol.* **A7** 2332 (1989).
10. B. Goranchev, K. Schmidt, and K. Reichelt, *Thin Solid Films* **149** 177 (1987).
11. E. Staryga, A. Lipinski, S. Mitura, and Z. Has, *Thin Solid Films* **145** 17 (1986).
12. D.R. McKenzie, R.C. McPhedran, L.C. Botten, N. Savvides, and R.P. Netterfield, *Appl. Opt.* **21** 3615 (1982).
13. N. Savvides, *Thin Solid Films*, **163** 13 (1988).
14. D.B. Kerwin, I.L. Spain, R.S. Robinson, B. Daudin, M. Dubus, and J. Fontenille, *Thin Solid Films* **148** 311 (1987).
15. M.J. Mirtich, D.M. Swec, and J.C. Angus, *Thin Solid Films* **131** 245 (1985).
16. A. Grill, B.S. Meyerson, V.V. Patel, J.A. Reimer, and M.A. Petrich, *J. Appl. Phys.* **61** 2874 (1987).
17. J.A. Woollam, V. Natarajan, J. Lamb, A.A. Khan, G. Bu-Abbud, D. Mathine, D. Rubin, R.O. Dillon, B. Banks, J. Pouch, D.A. Gulino, S. Domitz, D.C. Liu, and

- D. Ingram, *Thin Solid Films*, **119** 121 (1984).
18. F.M. El-Hossary, D.J. Fabian, C.J. Sofield, *Thin Solid Films* **157** 29 (1988).
 19. N. Savvides, *J. Appl. Phys.* **59** 4133 (1986).
 20. F.W. Smith, *J. Appl. Phys.* **55** 764 (1984).
 21. K. Enke, *Thin Solid Films* **80** 227 (1981).
 22. C. Weissmantel, K. Bewilogua, K. Breuer, D. Dietrich, U. Ebersbach, H.-J. Erler, B. Rau, and G. Reisse, *Thin Solid Films* **96** 31 (1982).
 23. W. Scharff, K. Hammer, O. Stenzel, J. Ullman, M. Vogel, T. Frauenheim, B. Eibisch, S. Roth, S. Schulze, and I. Muhling, *Thin Solid Films* **171** 157 (1989).
 24. J. Ishikawa, Y. Takeiri, K. Ogawa, and T. Takagi, *J. Appl. Phys.* **71** 2509 (1987).

Figure Captions

Figure 1. Spectral transmittance versus flow rate of H₂; thickness of all films is 500 Å; sputtering power is 200 W; total pressure is 10 mTorr.

Figure 2. Total solar and visible transmittance versus the fraction of H₂ flow in the Ar-H₂ mixture; thickness of all films is 500 Å; sputtering power is 200 W; total pressure is 10 mTorr.

Figure 3. Total solar and visible transmittance versus sputtering power; thickness of all films is 500 Å; total pressure is 10 mTorr.

Figure 4. Film stress measured by substrate bending versus H₂ flow rate; sputtering power is 200 W; total pressure is 10 mTorr.

Figure 5. Hardness measured by displacement microindenter versus H₂ flow rate; sputtering power is 200 W; total pressure is 10 mTorr.

Figure 6. Film stress measured by substrate bending versus sputtering power; total pressure is 10 mTorr.

Figure 7. Hardness measured by displacement microindenter versus sputtering power; total pressure is 10 mTorr.













