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Optical properties of "diamondlike" carbon films: An ellipsometric study

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The index of refraction and extinction coefficient are measured as a function of wavelength from 254 to 633 nm using reflection-null ellipsometry. It is shown that both rf glow-discharge-deposited and ion-beam-sputtered films have the same values of n and k over the measured wavelength range. Calculated values of absorption coefficient indicate that the absorption edge is not reached even at near ultraviolet wavelengths. Thermal cycling up to 500 °C does not change the optical properties significantly.

I. INTRODUCTION

Diamondlike *a*-carbon films are distinguishable from other forms of carbon films because of their unusual properties. These properties often include (but are not restricted to) partial optical transparency in the visible, low infrared (IR) absorption, high electrical resistivity, good adhesion to diverse substrates, resistance to corrosive chemicals, and hardness.[1]

Carbon films with these properties were first produced by Aisenberg and Chabot using ion-beam techniques.[2] Since then attempts have been made to deposit such films using a number of other techniques, such as cracking of hydrocarbons in a glow discharge,[3–5] ion-beam sputtering from a carbon target,[6] etc. Amorphous carbon films produced by these various techniques are in general smooth, hard, and semitransparent, but are not characterized uniquely and exhibit a wide range of physico-chemical properties.

The optical properties of these films are of particular importance, since their other properties make them potentially ideal for use as optical elements in high-powered lasers.[7] They have also been studied as antireflection (AR) coatings for solar cells.[8] There are, however, considerable discrepancies in the reported optical properties of this material. While most are said to be optically transparent in the visible, some films have been found to be "black and featureless,"[9] and optically absorbing,[10] although still characterized by a hard and smooth surface. Meyerson and Smith[11] conclude that optical properties of *a*-carbon films depend in a significant way on the amount and bonding of incorporated hydrogen. In contrast McKenzie *et al.*[12] have, recently, arrived at opposite conclusions for their dc-sputtered *a*-carbon films: They have noticed a marked decrease in absorption both in the visible and near-infrared regimes with increasing partial pressure of hydrogen in the sputtering gas. Moreover, this decrease in absorption is concurrent with an increase in the resistivity of the sputtered films over 8 orders of magnitude from 10^{-2} Ω cm to greater than 10^{6} Ω cm.

Although the wide range of optical (and other) properties of diamondlike carbon films could be attributed to the diversity of their preparation techniques, it must be admitted that little data (particularly optical) exists on well-characterized samples. Our research program aims at a thorough characterization of high resistivity *a*-carbon films. We have reported the results of capacitance and conductance measurements on *a*-carbon—Si metal-insulator semiconductor for structures,[13–15] as well as Raman scattering[16] and x-ray-photoelectron spectroscopy.[17] In this paper we report what we believe to be the first ellipsometric measurements on two different kinds of diamondlike carbon films: The glow-discharge-deposited films and the ion-beam-sputtered films both in as-deposited as well as annealed samples. Data on a few dc-sputter-deposited films are also reported. Emphasis is placed on accurately determining the optical refractive indices and extinction coefficients as a function of wavelength.

II. SAMPLE PREPARATION

For ion-beam sputtering, a carbon target and argon ions from a source developed as a space propulsion thruster were used. The apparatus has been described in detail elsewhere.[18] Silicon wafers of 3 in. diam, used as substrates, were loaded into the diffusion-pumped (10^{-6}-Torr) deposition chamber and cleaned *in situ* for 60 sec with an ion-beam etch. The etching time was chosen to be sufficient to completely remove the thin ($\sim$30-Å) layer of natural oxide from the wafer surface. This was necessary so one could use the two-phase model of ellipsometry. During deposition the beam current was 55 mA at 1 kV with a beam diameter of 10 cm. There was no deliberate voltage-biasing or heating of the substrate. The deposition rate was found to be about 10—15 Å/min. The resulting films were pale yellow, shiny smooth, and hard, with excellent adhesion to the substrate.

For plasma-deposited films, a Perkin-Elmer Model-3140 sputtering system was used in the sputter-bias mode. Again the substrates were cleaned *in situ* to remove the natural oxides. A discharge was generated in methane gas with an rf power of about 20 W. Substrates were at a near-zero bias and were at room temperature. In this case the deposition rates were approximately 100 Å/min. The resulting films were shiny blue, hard, and very smooth.

A few samples were also made by dc sputtering of a graphite target in an Ar ambient. 1-in.-diam Si wafers were used as substrates in this case. In this simple, mechanically pumped setup, *in situ* cleaning was not possible. Chemical cleaning was employed to reduce the effects of natural oxides as much as possible. Prior to deposition, wafers were degreased in trichloroethylene, acetone, and methanol, etched in HCl for 30 sec, and then followed by another cleaning cycle. Each processing step was preceded by a rinse in deionized (DI) water and a blow dry in filtered dry N_2. During deposition the electrode voltage was 1 kV with a current of 10 mA and a chamber pressure of 0.1 Torr. Under these conditions the deposition rate was approximately 12 Å/min. The resulting films were shiny, hard, and brownish black in color. After deposition each wafer was diced into 1×1 cm^2 samples for use in different experiments. A series of samples from each wafer (ion beam and plasma deposited only) were annealed up to 500 °C. High-purity hydrogen was used as annealing ambients.

III. EXPERIMENTAL DETAILS

A Gaertner Model L-119X modified null ellipsometer fitted with ultraviolet focusing lenses was used in a polarizer sample-compensator analyzer configuration. Rochon and Glan Thompson polarizers were used in conjunction with a Babinet Soleil compensator. The angle of incidence could be set to within 0.02°, while the relative accuracy in the polarizer and analyzer angles was 0.05°. A He-Ne laser was used for the 6328-Å wavelength, and a mercury arc lamp fitted with an ultraviolet collimeter was used to get measurements in the rest of the wavelength range. At each wavelength at least six angles of incidence were used. All measurements were four zone. The ellipsometer was aligned using a procedure of Azzam and Bashara.[19] The ellipsometric parameters ψ and Δ were obtained by feeding the experimental data to a previously described[20] computer program that automatically compensates for systematic errors and misalignments in optical components, etc., and yields calibrated values of these parameters. The values of ψ and Δ thus obtained were used in a recently described computer program[21] which uses a Marquardt algorithm to minimize the sum of squares ($\sum\sigma^2$, σ is the deviation) of deviations between experimental and theoretical values of the ellipsometric parameters and calculates the refractive indices, extinction coefficients, and the film thickness based on a given model. Based on experience with ellipsometric measurements on numerous different materials and geometries, a value of $\sum\sigma^2$ on the order of 5 or less for our samples represents excellent results.[19,21]

IV. RESULTS AND DISCUSSION

There are two most commonly used models in ellipsometry: The two-phase model in which the system is assumed to consist of a thin film on top of a substrate (with known optical constants), and the three-phase model in which a very thin interfacial layer of materials having optical properties different from either the substrate or the film is assumed to exist. The three-phase model introduces three more parameters (refractive index, extinction coefficient, and the thickness of the interfacial layer), and hence requires more extensive measurements. It is, however, essential from a more realistic point of view: The presence of natural oxides, transitional layers, and/or heavy surface damage can all lead to graded interfaces that are several angstroms wide. We took care of this problem in two ways: (1) All efforts were made to remove the natural oxides, *in situ* or otherwise, and (2) multiple-wavelength, multiple—angle-of-incidence measurements were taken to enhance the accuracy of the model fit (by reducing parameter correlations) in the usual two-phase analysis, and to also make a check on these calculations by performing the three-phase—model calculations in one of the samples.

To further improve the reliability of the data, we did not use the optical constants for Si from the literature, but rather measured these values for samples taken from substrate wafers. These values are listed in Table I.

Table II gives the details about sample preparation, annealing temperature (annealing time is 15 min for all samples), and the values of $\sum\sigma^2$ as obtained from the multiple-wavelength, multiple—angle-of-incidence analysis. It is obvious that we were able to get very good fit of the data to the conventional two-phase model of ellipsometry. As a further check we also analyzed the data assuming a three-phase model for one sample (no. 6). For this calculation we assumed an initial thickness of 25 Å for interfacial SiO_2; the thickness was then varied as a parameter in computer calculations. The data converged to the same values as reported here with interfacial oxide thickness of 0.06 Å. This is a strong indication that we have been successful in eliminating the effects of natural oxides on Si wafers.

Figure 1 shows the refractive indices of all the samples plotted as a function of wavelength. The wavelengths at which the measurements were taken are marked by arrows on the graph. Data points are shown displaced along the wavelength axis for clarity. Note that all data points lie within a narrow strip about $\Delta n = 0.2$ wide. This demonstrates that the refractive indices of all samples used in

TABLE I. Experimentally measured optical properties of *p*-Si on the (111) face used in the two-phase model of ellipsometry.

Wavelength λ (Å)	Refractive index n	Extinction coefficient k
2536	1.63 ± 0.03	-3.63 ± 0.02
3131	4.85 ± 0.02	-3.52 ± 0.03
3650	6.79 ± 0.01	-2.60 ± 0.03
4358	4.83 ± 0.02	-0.25 ± 0.01
5460	4.113 ± 0.005	-0.01 ± 0.00
6328	3.889 ± 0.005	

TABLE II. Description of samples used in this study. $\sum\sigma^2$ represents the sum of the squares of the deviation of experimental data from that of theoretically calculated values. Each value of $\sum\sigma^2$ in the column represents, on the average, a sum of 60 quantities. Significance of $\sum\sigma^2$ as an indicator of a good fit between experiment and theory is complicated (Refs. 19 and 21), but numbers less than about 5 represent excellent results. (Parentheses denote designations used in other publications.)

Sample no.	Preparation method	Film thickness (Å)	Annealing Conditions	$\sum\sigma^2$
1 (JW122)	Ion-beam-sputtered	1380±15	As-deposited	1.27
2 (NA no. 2)	Plasma-deposited	1265±22	As-deposited	0.20
3 (HA no. 7)	Ion-beam-sputtered	1362±31	Annealed in H_2 at ~300 °C	2.25
4 (HA no. 8)	Ion-beam-sputtered	1518±32	Annealed in H_2 at ~400 °C	2.47
5 (HAS no. 7)	Ion-beam-sputtered	1403±32	Annealed in H_2 at ~500 °C	0.96
6 (HAS no. 2)	Plasma-deposited	1204±16	Annealed in H_2 at ~500 °C	0.76

our study are the same to within 5—10% of each other regardless of their method of preparation and regardless of their annealing temperature. The same sort of behavior is indicated in Fig. 2, which shows the experimentally determined values of the extinction coefficients plotted as a function of the wavelength. Almost all values of k are seen to be within a narrow strip of $\sim\Delta k = -0.06$ wide. This suggests that both preparation techniques produce films having the same structure, which does not change much upon annealing at a low to medium range of temperatures. What is surprising is a total lack of effect of hydrogen on the optical properties, especially in view of the discussion presented earlier. Admittedly, we have a small range of wavelengths, but we feel that it is enough to indicate any large-scale effects of hydrogen incorporation into the structure of a-carbon. We note especially the absence of any systematic differences in the optical properties of sample no. 1 (which is ion-beam-sputter prepared) and sample no. 6 (which is prepared by cracking of methane followed by annealing in hydrogen gas at 500 °C). Another feature of this diagram is the relatively rapid increase in the extinction coefficients up to 313.1 nm, followed by only a minor increase at 253.6 nm (the slope seems to change but unfortunately we do not have data beyond this point). This results in absorption coefficient values that change by little more than an order of magnitude over this wavelength range.

Experimental values of the extinction coefficient were used to calculate the absorption coefficient α. Figures 3 and 4 are plots of calculated values of α versus photon energy for ion-beam- and plasma-deposited films. In each figure we show data for only two samples, the as-deposited sample and one that has been annealed at the highest temperature used in this study. There is a slight

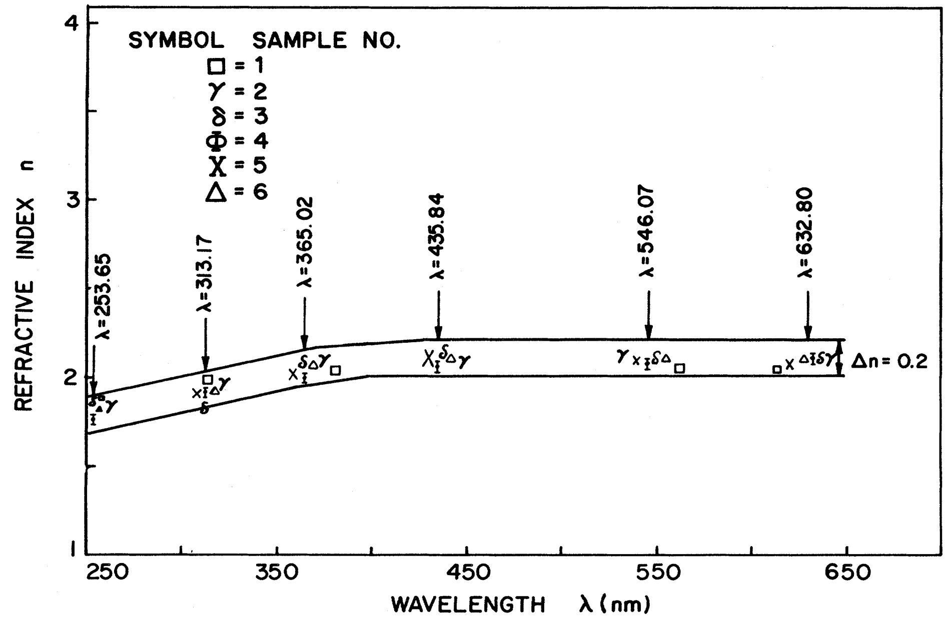

FIG. 1. Refractive index of as-prepared and annealed diamondlike carbon films as a function of wavelength. Wavelengths at which the data are taken is indicated by arrows. Size of the symbols is a rough measure of the relative errors.

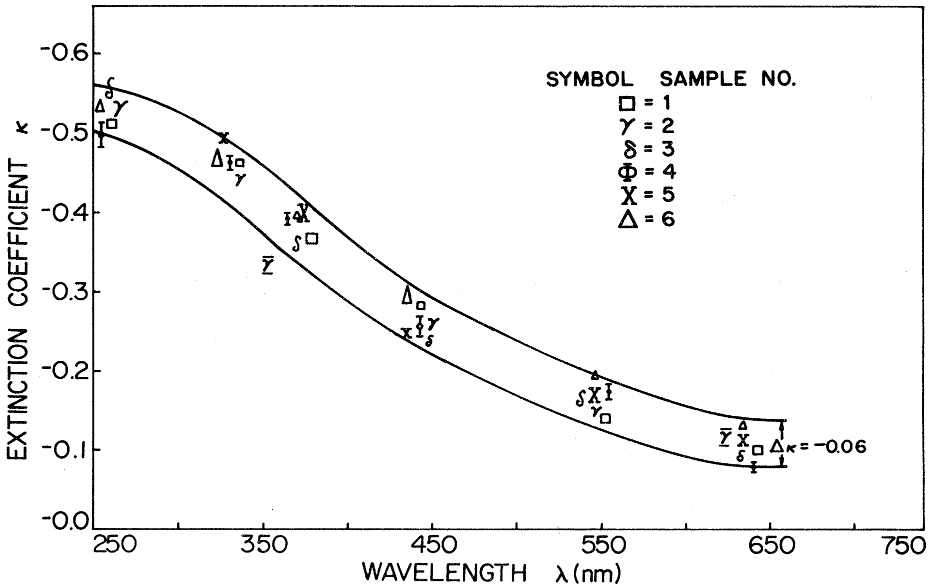

FIG. 2. Extinction coefficients as a function of wavelength for the same samples as in Fig. 1. Wavelengths at which the data are taken are indicated in Fig. 1.

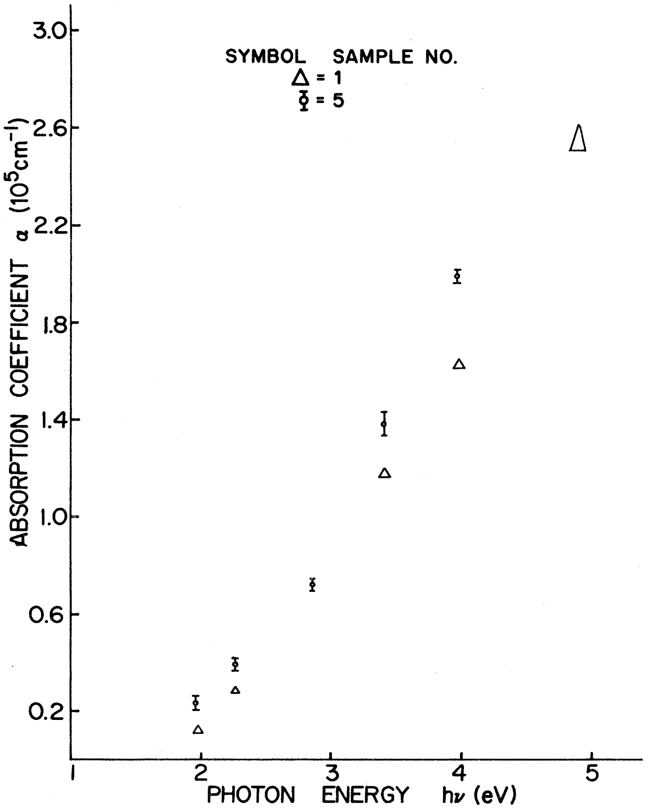

FIG. 3. Absorption coefficient α of as-prepared and 500 °C annealed samples of ion-beam-sputtered *a*-carbon films as a function of photon energy. Note the slight but consistent increase in the absorption coefficient of the annealed specimen at all the measured points.

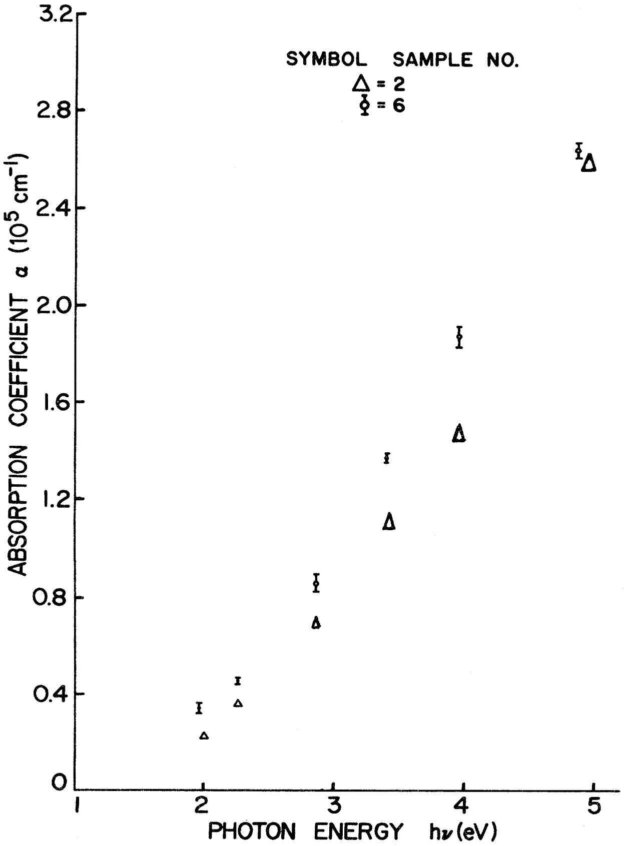

FIG. 4. Absorption coefficient α of as-prepared and 500 °C annealed samples of plasma-deposited *a*-carbon films as a function of photon energy. Note that the relative increase in absorption of the annealed sample is the same as that for the ion-beam-sputter—deposited sample shown in Fig. 3.

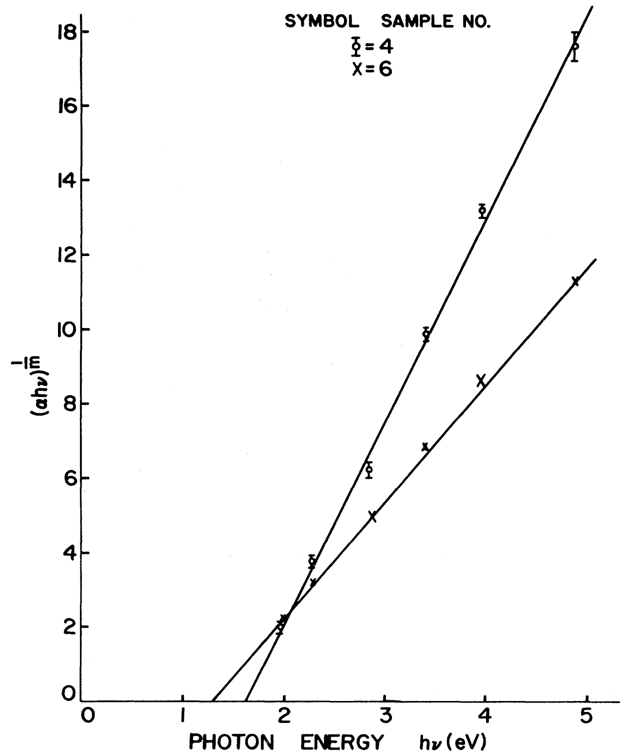

FIG. 5. $(\alpha h\nu)^{1/2}$ vs $h\nu$ plotted for ion beam- and plasma-deposited samples. Both samples have been annealed (see Table II).

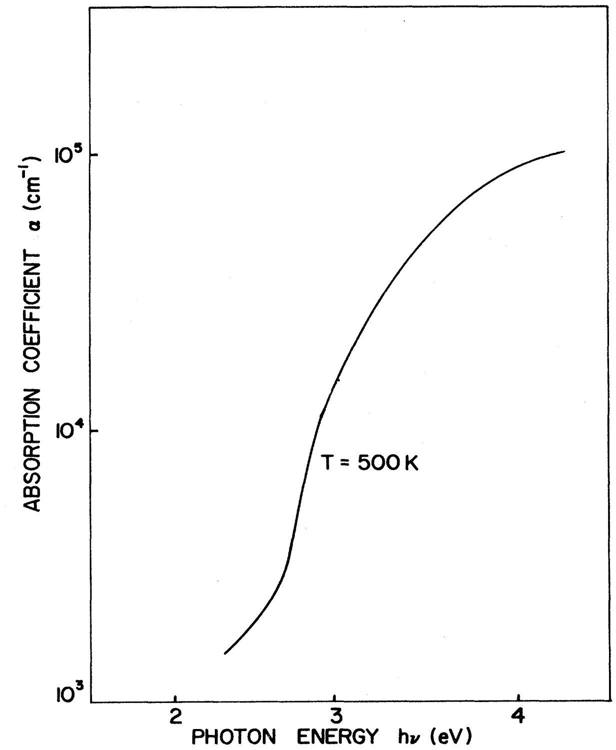

FIG. 6. Absorption-coefficient—vs—photon-energy plot of one of the samples of Ref. 23. Note the lower absorption at longer wavelengths and higher absorption at shorter wavelengths relative to the samples studied in this report. Temperature indicated is the substrate deposition temperature.

but unmistakable increase in the absorption coefficients of the annealed samples. Furthermore, the relative magnitude of absorption and its increase with annealing is the same in both types of films.

It is well known that in amorphous solids, interband optical absorption can be represented as[22]

$$\alpha = \text{const}(h\nu - E_{\text{op}})^m / h\nu$$

where E_{op} is the optical band gap and m is an exponent which depends on the nature of the band edges. The most frequently encountered value of the exponent is $m=2$, which indicates the parabolic nature of the band edge. In Fig. 5 we show a plot of $(\alpha h\nu)^{1/m}$ vs $h\nu$ for two of our samples. For the ion-beam-deposited sample a good fit to a straight line is obtained for $m=1.7$ while for the plasma-deposited film, $m=2$ yields a good fit. From the intercepts of these graphs on the energy axis, optical band gaps are found to be $E_{\text{op}} \sim 1.6$ and 1.24 eV for the ion-beam- and plasma-deposited films, respectively. As mentioned earlier, data was taken on a few dc-sputtered samples also. Optical constants determined for a typical sample are listed in Table III. It is clear that the dc-sputtered films have considerably lower values of n and higher values of k than either the ion-beam- or the plasma-deposited films at these wavelengths. This suggests that dc-sputtered films may be structurally different from the diamondlike a-carbon films prepared by ion-beam sputtering and plasma deposition.

V. COMPARISON WITH LITERATURE

As mentioned earlier, very little optical data is available on these films, especially in the visible range. In this section we will compare our results with other published re-

TABLE III. Refractive index and extinction coefficient of dc-sputtered a-C films for a few wavelengths.

Wavelength λ (Å)	Refractive index n	Extinction coefficient k	Thickness d (Å)
4358	1.40±0.07	−0.217±0.004	664±57
5460	1.37±0.06	−0.167±0.006	664±57
6328	1.33±0.05	−0.128±0.008	664±57

sults. Anderson[23] has determined the optical-absorption coefficient α from a study of optical transmission in glow-discharge-prepared samples of *a*-carbon. For comparison we reproduce the α—versus—photon-energy curve for his *least* absorbing sample in Fig. 6. We note that between 2.25 and 4 eV, α increases from $\sim 2\times 10^3$ to 10^5 cm^{-1}, i.e., an increase of almost 2 orders of magnitude. By comparison, in our *most* absorbing sample, no. 6 (see Table II), α increases by only a factor of 6 in this energy range. Even in the entire energy range (1.96—4.9 eV) the total increase in the absorption coefficient is about an order of magnitude.

Meyerson and Smith[11] have calculated α by studying optical absorption in glow-discharge-prepared *a*-carbon films using a spectrophotometer. They report values of α rising from $\sim 10^4$ to $\sim 10^5$ cm^{-1} from 2.25 to 3.9 eV for their lesser absorbing sample (substrate deposition temperature less than 250 °C). Their results are therefore intermediate to those obtained by Anderson and the ones reported here. Another significant observation relates to the values of the optical gap in these films. Both Anderson and Meyerson report values of this parameter obtained by extrapolating $(\alpha h\nu)^{1/2}$-vs-$h\nu$ plots to zero absorption. These values vary from 1.5 to 2.6 eV (Anderson) and from 0.9 to 2.0 eV (Meyerson) depending on the substrate temperature. We notice that although our samples exhibit lesser variation in α in a greater energy range, the optical band gap we observe is much less than the higher values (2.6 and 2.0) obtained by these authors. This apparent contradiction can be resolved if one realizes that the conventional approach of extrapolating $(\alpha h\nu)^{1/m}$-vs-$h\nu$ curves works best when the band-tailing effects are small and one scans an energy range sufficiently greater than the nominal value of the optical band gap, as indicated by a change in the value of the absorption coefficient α of several orders of magnitude. Even in Anderson's case ($E_{\text{op}} \sim 2.6$ eV) the change in α is about 2 orders of magnitude, while Meyerson ($E_{\text{op}} \sim 2.0$ eV) has α changing by an order of magnitude. In this work ($E_{\text{op}} \sim 1.6$ eV), although the energy range is much greater, α changes about an order of magnitude. It is therefore highly likely that none of the investigations have truly reached the band edge and the extrapolation is yielding the value of the band tails rather than the true optical gap. We thus propose that the optical band gap of the diamondlike films is far greater than previously suspected, with extensive band tails that reach as far as approximately an electron volt from the band edges. Accurate values of the absorption coefficients in the vacuum-ultraviolet region are needed to verify this tentative conclusion. However, some indication that diamondlike carbon films may have such a high value of the optical band gap is already available: Zelez[24] and Ichinose *et al.*[25] have recently reported optical band gaps of 3.05 and 3.1 eV in their diamondlike carbon films.

VI. SUMMARY AND CONCLUSIONS

We have presented precise values of the optical constants of diamondlike and dc-sputtered *a*-carbon films in a fairly wide range of energies. We find that both rf- and ion-beam-sputtered samples have nominally the same values of n and k, while dc-sputtered films have substantially different values. Annealing experiments indicate that low-temperature annealing does not induce appreciable changes in the optical constants of these films. However, there is a slight systematic increase in k values (and hence also in the absorption coefficient) of 500 °C annealed samples relative to the as-prepared films. This indicates that the threshold for structural changes is around 500 °C. This result is consistent with the conclusions drawn from a recent Raman scattering study[16] of the same films. This study indicates that both ion-beam- and plasma-deposited films undergo a structural change somewhere between 450 and 500 °C. Moreover, no differences are noticed in the behavior of samples annealed in N_2 as compared to those annealed in H_2. Naiesh and Nowak[26] have observed a broad exothermic peak in a differential-scanning-calorimetry (DSC) experiment at around 550 °C. This also signals a structural change at around that temperature. However, since their films were deposited by glow discharge from methane, they attribute this peak to the release of hydrogen. This mechanism does not explain our (and Raman scattering) results on ion-beam-deposited films unless one assumes that ion-beam-deposited films have the same amount of incorporated hydrogen as do the rf glow-discharge-deposited films, which is unlikely.

It would be interesting to extend the ellipsometric study to samples annealed at higher ($500 < T < 1000$ K) temperatures, and to samples annealed in N_2, to see if the optical properties of these films change more drastically at higher temperatures as indicated by some nonellipsometric measurements.[16,27] At the same time the energy range must also be extended to the vacuum-ultraviolet region to obtain more reliable and reproducible values of the optical band gap.

It is conceivable that the large differences in the reported values of the absorption coefficient (e.g., between this study and results in Refs. 11 and 21) are related to the presence of hydrogen or to differences in structure. We have made Auger and electron spectroscopy for chemical analysis profiles and scans[17] which show that the only impurity in the samples is a thin layer of physisorbed oxygen on the top surface. It is very unlikely that this oxygen layer influences the magnitude of the absorption coefficient. Hydrogen was present (as determined by activation analysis) in similarly prepared samples. Thus, hydrogen and/or structure may be influencing the relative magnitudes of absorption in samples made by different research groups.

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[1] E. G. Spencer, P. H. Schmidt, D. C. Joy, and F. J. Sansalone, Appl. Phys. Lett. 29, 118 (1976).

[2] S. Aisenberg and R. Chabot, J. Appl. Phys. 42, 2953 (1971).

[3] D. S. Whitmell and R. Williamson, Thin Solid Films 35, 255 (1976).

[4] L. Holland and S. M. Ojha, Thin Solid Films 38, L17 (1976).

[5] S. Berg and L. P. Anderson, Thin Solid Films 58, 117 (1979).

[6] C. Weissmantel, in *Proceedings of the 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces, 1977*, edited by R. Dobrozemsky, F. P. Ruedenaur, A. Breth, and F. P. Viehboeck (Berger, Vienna, 1978), p. 1538.

[7] S. Aisenberg and M. Stein, National Bureau of Standards (NBS) Special Publication 620, American Society for Testing and Materials STP-759, 313 (1981) (unpublished).

[8] T. J. Moravec and J. C. Lee, Solar Energy Research Institute (Colorado) Technical Progress Report, SERI Contract No. SX-0-9010-3 (unpublished).

[9] D. S. Whitmell and R. Williamson, Thin Solid Films 35, 255 (1976).

[10] L. Holland and S. M. Ojha, Thin Solid Films 38, L17 (1976).

[11] B. Meyerson and F. W. Smith, J. Non-Cryst. Solids, 35-36, 435 (1980).

[12] D. R. McKenzie, R. C. McPhedran, L. C. Botten, N. Savvides, and R. P. Netterfield, Appl. Opt. 21, 3615 (1982).

[13] A. A. Khan, J. A. Woollam, Y. Chung, and B. Banks, Electron Devices Lett. EDL-4, 146 (1983).

[14] A. A. Khan, J. A. Woollam, and Y. Chung, Solid-State Electron. (in press).

[15] A. A. Khan. J. A. Woollam, and Y. Chung, in *Proceedings of the 16th Biennial Conference on Carbon, American Carbon Committee, July 1983,* edited by G. B. Engle and R. J. Price (American Carbon Society, San Diego, 1983).

[16] R. O. Dillon and J. A. Woollam, in *Proceedings of the 16th Biennial Conference on Carbon, American Carbon Committee, July 1983,* Ref. 15.

[17] D. Liu, R. O. Dillon, and J. A. Woollam, *Proceedings of the 16th Biennial Conference on Carbon, American Carbon Committee, July 1983,* Ref. 15.

[18] B. A. Banks and S. K. Rutledge, U. S. National Aeronautics and Space Administration Report No. NASA-TM82873.

[19] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977).

[20] J. R. Adams and N. M. Bashara, Appl. Opt. 15, 3179 (1976).

[21] G. H. Bu-Abbud and N. M. Bashara, Appl. Opt. 20, 3020 (1981).

[22] E. A. Davis, in *Electronic and Structural Properties of Amorphous Semiconductors, Proceedings of the 13th Session of the Scottish Universities Summer School in Physics, 1972,* edited by P. G. LeCombre and J. Mort (Academic, London, 1973).

[23] D. A. Anderson, Philos. Mag. 35, 17 (1977).

[24] J. Zelez, RCA Rev. 43, 665 (1982).

[25] Y. Ichinose and F. Shinokawa, *Proceedings of the 16th Biennial Conference on Carbon, American Carbon Committee, July 1983,* Ref. 15.

[26] A. R. Nyaiesh and W. B. Nowak, J. Vac. Sci. Technol. A1, 308 (1983).

[27] F. W. Smith, M. Turner, and N. Gilbert, Bull. Am. Phys. Soc. 27, 146 (1982).