

Arc-evaporated carbon films: Optical properties and electron mean free paths

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(Received 21 November 1984)

The real and imaginary parts of the complex refractive index, $\tilde{n}(\omega) = n(\omega) + ik(\omega)$, of arc-evaporated carbon films have been obtained over the range of photon energies $\hbar\omega$ from 0.5 to 62.0 eV. Values of $k(\omega)$ obtained from transmission measurements in this energy range were combined with values of $k(\omega)$ from the literature in the infrared and soft-x-ray regions. A Kramers-Kronig analysis then yielded the values of $n(\omega)$. The density of the arc-evaporated carbon films was found to be $1.90 \pm 0.05 \text{ g cm}^{-3}$ by the "sink-float" method, and their thicknesses were determined optically. A sum-rule calculation yielded the effective numbers of valence and core electrons to be 4.2 and 1.8, respectively. The experimental values determined for $\tilde{n}(\omega)$ have been used to estimate values of the inelastic mean free path $\Lambda(E)$ for electrons of energy E from 200 to 3000 eV in amorphous carbon. Good agreement is found between $\Lambda(E)$ and experimentally determined values of electron attenuation length $L(E)$ from the literature.

I. INTRODUCTION

Arc-evaporated carbon films can be produced which are homogeneous and have great mechanical stability, even when they are extremely thin. They can be produced as coatings or as self-supporting films. In addition, carbon does not oxidize under normal atmospheric conditions. These properties have resulted in a number of uses for thin, arc-evaporated carbon films, including protective coverings on metal films¹ and substrates in electron microscopy.² The utilization of carbon as a protective covering or as a substrate in optical experiments requires a knowledge of its optical properties at the photon energy being used. In addition, the calculation of electron mean free paths in carbon or the energy deposition by ionizing particles traversing the material requires a knowledge of the optical properties of the carbon used, over the whole spectrum of photon energies.

There is an extensive literature on carbon. However, carbon exists in many different forms with widely differing optical properties. The most extensive compilation of optical properties for carbon¹ combines data for different forms of the material. Even for arc-evaporated carbon films, the optical properties can depend markedly on the conditions of preparation.^{3,4}

The response of a material to photons of energy $\hbar\omega$ can be characterized by a complex refractive index $\tilde{n}(\omega) = n(\omega) + ik(\omega)$ or by a complex dielectric function $\epsilon(\omega)$ where $\epsilon(\omega) = \tilde{n}(\omega)^2$. The refractive index $n(\omega)$ is related to the extinction coefficient $k(\omega)$ through a Kramers-Kronig dispersion relation,⁵

$$n(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega' k(\omega')}{(\omega')^2 - \omega^2} d\omega'. \quad (1)$$

Thus if $k(\omega)$ is known over the whole range of photon energies, $n(\omega)$ can be calculated at any energy $\hbar\omega$.

Optical data on arc-evaporated carbon already exist from transmission measurements in the ir (Ref. 2) and

extreme-uv (xuv) to soft-x-ray (Ref. 6) regions and from ellipsometric measurements in the ir to visible.⁷ These data cover broad energy ranges, including data on either side of the carbon K edge. We present here the optical properties of arc-evaporated carbon from the near ir to the xuv (0.5 to 62 eV). Our data cover an energy range not previously studied, while overlapping the existing ir and soft-x-ray data. By combining our data on $k(\omega)$ with the previously existing data, we show that the $k(\omega)$ sum rule is valid. We then use the optical properties to calculate the inelastic mean free path of low-energy electrons in arc-evaporated carbon.

II. EXPERIMENTAL

A. Preparation and measurement

We used self-supporting arc-evaporated carbon films to obtain $k(\omega)$ from transmittance measurements over the photon energy range from 0.5 to 62.0 eV. In addition, various measurements yielding $n(\omega)$ and/or $k(\omega)$ were made on arc-evaporated carbon films on glass substrates, in the photon energy range from 0.5 to 3.1 eV.

Carbon films were prepared by arc-evaporation of high-purity carbon rods in a vacuum evaporator. For the carbon films on glass substrates, the carbon was deposited at a rate of $\sim 0.5 \text{ nm sec}^{-1}$ onto clean glass slides at room temperature. In the photon energy range from 0.5 to 3.1 eV, transmittance was measured as a function of film thickness using a Cary model no. 14 spectrometer. Film thicknesses were obtained, after all transmission measurements were completed, by an interferometric technique.⁸ For each photon energy, the values of n and k were obtained from Fresnel's equations for a finite film thickness. A least-squares-fitting procedure was used to obtain n and k from an experimental plot of transmittance versus film thickness. Film thicknesses ranged from 25 to 250 nm for these measurements. In the energy range from 0.6 to 3.1 eV, thick films deposited on glass slides were also used to obtain $n(\omega)$ independently by means of ellipsometric mea-

surements.⁷ The $k(\omega)$ values were too small to be obtained with good accuracy by this method.

For the production of self-supporting carbon films, the glass slides were covered with a film of soap solution.⁹ After carbon deposition, the carbon film was separated from the glass by floating it off onto the surface of cooled, distilled water. It was then picked up on a holder with a 1-cm-diam aperture. The thicknesses of these films were determined by an optical method¹⁰ to be in the range from 100 to 220 nm. The method involved measuring transmittance using photons from a He-Ne laser ($\lambda = 632.8$ nm). Film thickness was then obtained from a curve of transmittance versus thickness for this wavelength which had been calibrated using a quartz-crystal thickness monitor. Because the quartz-crystal monitor measures changes in mass, but not thickness, an accurate determination of the density of the films was necessary. Their density, ρ , was found to be (1.90 ± 0.05) g cm⁻³ by the sink-float method using known mixtures of carbon tetrachloride ($\rho = 1.594$ g cm⁻³) and bromoform ($\rho = 2.889$ g cm⁻³). An absolute calibration of the thickest films was obtained interferometrically. Using the self-supporting arc-evaporated carbon films, measurements of transmittance as a function of film thickness were obtained from 0.5 to 3.1 eV using the Cary model no. 14 spectrometer, while transmittances were obtained for the thinnest films from 3.1 to 12.4 eV using a Seya-Namioka spectrometer and from 9.5 to 62 eV using a McPherson model no. 247 grazing incidence monochromator. The transmittance measurements from 3.1 to 62 eV yielded accurate values for $k(\omega)$ only, since the transmittance values in this energy range are not very sensitive to the $n(\omega)$ values.

It is well known³ that the optical properties of arc-evaporated carbon films depend on the exact conditions employed in their preparation. For our films, prepared as described, the $k(\omega)$ values reported over the energy range 0.5 to 62.0 eV have uncertainties of $\pm(10-15)\%$, depending on the photon energy. Measured values of $n(\omega)$ have an associated uncertainty of $\pm 5\%$.

Below 0.5 eV we found that $k(\omega)$ becomes very small, as was previously demonstrated by Knoll and Geiger.² This means that for the long wavelengths in the ir and for $k(\omega)$ small, very thick films (> 500 nm) are required in order to obtain $k(\omega)$ accurately. However, even though for relatively thin films (< 200 nm) arc-evaporation of carbon produces amorphous carbon films, as the film thickness increases "graphitization" occurs. In addition, when $k(\omega)$ is very small, the correction term in the expression for transmittance due to reflectance at the film surfaces becomes critical. Since $n(\omega)$ is only known to $\pm 5\%$, this severely limits the accuracy with which small $k(\omega)$ values can be deduced. Thus we were unable to obtain accurate $k(\omega)$ values corresponding to thin arc-evaporated amorphous carbon films from transmittance measurements below 0.5 eV.

B. Evaluation of the data

A compilation of k values over the whole range of optical frequencies was made. The variation of k with photon

energy $\hbar\omega$ is shown in Fig. 1. Below 0.5 eV the k values are due to Knoll and Geiger.² Above 62 eV the k values are due to Fomichev and Zhukova⁶ scaled to a density of 1.90 g cm⁻³ from the apparent value¹¹ for their films of 2.28 g cm⁻³. From their fit to the data between 62 and 283 eV and the required density scaling, we obtained

$$k(\omega) = 1.73 \times 10^4 (\hbar\omega)^{-3.25} \quad (2)$$

The data in Ref. 6 above the carbon K edge have been further reduced by 8% as suggested by examination of the compilation of high-energy absorption cross sections for carbon due to Hubbell.¹² Values of $k(\omega)$ from the carbon K edge up to 700 eV were thus given by

$$k(\omega) = 6.82 \times 10^6 (\hbar\omega)^{-3.75} \quad (3)$$

As a check on the overall consistency of the k values, the sum rule for $k(\omega)$ was evaluated,¹³ i.e.,

$$N_{\text{eff}}(\omega) = \frac{m}{\pi^2 n_0 e^2} \int_0^\omega \omega' k(\omega') d\omega', \quad (4)$$

where $N_{\text{eff}}(\omega)$ should approach 6, as $\omega \rightarrow \infty$. In this expression, $N_{\text{eff}}(\omega)$ is the effective number of electrons participating in absorption up to an energy $\hbar\omega$ and n_0 is the atomic density where $n_0 = N_0 \rho / A$, with N_0 equal to Avogadro's number and A the atomic weight of carbon. In calculating values of $N_{\text{eff}}(\omega)$, the values of $k(\omega)$ given in Fig. 1 were used for energies up to 700 eV. For energies above 700 eV, k was taken to decrease with photon energy as $(\hbar\omega)^{-4}$ as indicated both by Hubbell's compilation¹² and by the theoretical treatment of a free-electron gas. The values of $N_{\text{eff}}(\omega)$ obtained are shown in Fig. 2, and it is seen that a value of $N_{\text{eff}} = 6.0$ was obtained for $\hbar\omega \rightarrow \infty$, as required. To obtain the effective number of valence electrons as a function of photon energy, the data below the carbon K edge were extrapolated to higher energies, using Eq. (2) up to 700 eV and a $(\hbar\omega)^{-4}$ dependence

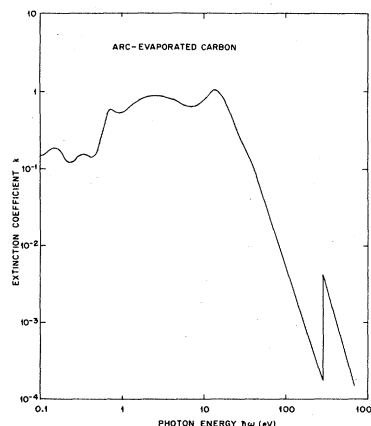


FIG. 1. Extinction coefficient, k , for arc-evaporated carbon films as a function of photon energy $\hbar\omega$. Below 0.5 eV, from Ref. 2; from 0.5 to 62 eV, from the present study, and above 62 eV, from Ref. 6, as explained in the text.

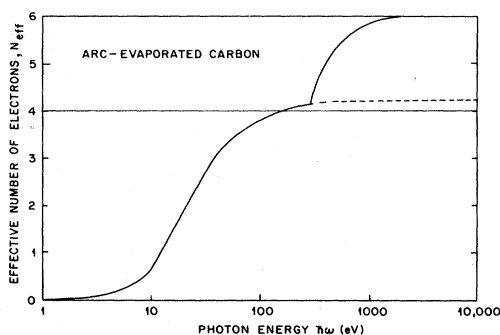


FIG. 2. Effective number of electrons per carbon atom, $N_{\text{eff}}(\omega)$, obtained from the extinction coefficient k as a function of photon energy $\hbar\omega$. $N_{\text{eff}}(\omega)$ is divided into valence and core electron contributions, as discussed in the text.

from 700 eV to infinite energy. By this procedure, in the high-energy limit the effective numbers of valence and core electrons are 4.2 and 1.8, respectively. This value for the effective number of K -shell electrons is consistent with the value 1.81 obtained from optical data on polystyrene⁵ and with the value of 1.72 determined from theoretical calculations of the oscillator strength for K -shell ionization.¹⁴ It should be noted that the effective number of valence electrons of 4.2 derives directly from the reported optical data scaled to a density of 1.90 g cm^{-3} . The effective number of core electrons was larger than 1.8 with use of the data reported in Ref. 6. The reduction of 8% which gave the required number of 1.8 core electrons and, hence, a total number of six electrons, was consistent with the rest of the data reported in the literature.¹² Furthermore, inclusion of the values of $k(\omega)$ above the K edge affects the values of $n(\omega)$, calculated by a Kramers-Kronig analysis, over the energy range from 0.5 to 62.0 eV by $\leq 0.1\%$. Thus the values used for $k(\omega)$ above the carbon K edge are unimportant as far as our reported $n(\omega)$ values are concerned.

A Kramers-Kronig analysis of the $k(\omega)$ data in Fig. 1

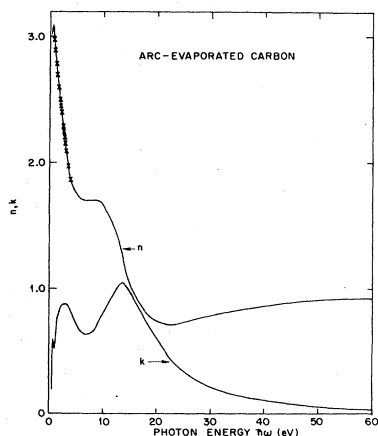


FIG. 3. Optical properties n and k of arc-evaporated carbon films as functions of photon energy $\hbar\omega$. For the refractive index n : —, from Kramers-Kronig analysis of k ; \times , independent measurements from present study and Ref. 7.

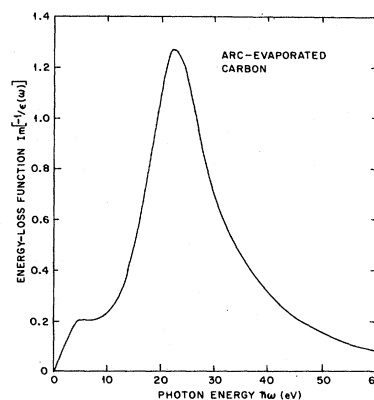


FIG. 4. Energy-loss function $\text{Im}[-1/\epsilon(\omega)]$ of arc-evaporated carbon films as a function of photon energy $\hbar\omega$.

was then performed using Eq. (1). The n values obtained between 0.5 and 60 eV are shown in Fig. 3. The values of n obtained independently from transmittance and ellipsometric measurements are shown to be in agreement with those obtained from the Kramers-Kronig analysis. A plot of the energy-loss function $\text{Im}[-1/\epsilon(\omega)]$, calculated from the n and k values shown in Fig. 3, is presented in Fig. 4. Values of $n(\omega)$ and $k(\omega)$ obtained experimentally are also shown in Table I.

III. APPLICATION OF DATA: ELECTRON MEAN FREE PATHS

Electron inelastic mean free paths are required in track structure calculations and in the analysis of the surface region of a solid by electron spectroscopies. However, electron inelastic mean free paths, Λ , or the related electron attenuation lengths, L , are difficult to measure for relatively low-energy electrons (~ 10 to $\sim 10^4$ eV) owing to their small values ranging from less than 1 nm to ~ 20 nm.

The inelastic mean free path for an electron of incident energy E is given by¹⁵

$$\Lambda^{-1} = \frac{me^2}{\pi\hbar E} \int \frac{dq}{q} \int \text{Im} \left[\frac{-1}{\epsilon(q, \omega)} \right] d\omega, \quad (5)$$

where $\hbar\omega$ and $\hbar q$ are the energy and momentum transfer to the medium, respectively. The limiting value as $q \rightarrow 0$ of $\text{Im}[-1/\epsilon(q, \omega)]$ gives

$$\text{Im}[-1/\epsilon(0, \omega)] \equiv \text{Im}[-1/\epsilon(\omega)]$$

which is the quantity determined optically and shown in Fig. 4 for arc-evaporated carbon.

To estimate $\text{Im}[-1/\epsilon(q, \omega)]$ from the optical properties requires a theoretical model for $\text{Im}[-1/\epsilon(q, \omega)]$. The model described in Ref. 16 extends the optical results to finite q so that the proper theoretical limit is obtained for large ω and q . The model should apply to any material. The parameters required to predict Λ are obtained by averaging over the optical energy-loss function. Specifi-

TABLE I. Real and imaginary parts, n and k , of the complex refractive index of thin, arc-evaporated carbon films.

| E (eV) | n | k |
|----------|-------|--------|
| 0.50 | 3.05 | 0.187 |
| 0.55 | 3.09 | 0.272 |
| 0.60 | 3.10 | 0.356 |
| 0.63 | 3.11 | 0.421 |
| 0.65 | 3.10 | 0.482 |
| 0.69 | 3.00 | 0.599 |
| 0.70 | 2.96 | 0.595 |
| 0.80 | 2.82 | 0.551 |
| 0.85 | 2.80 | 0.533 |
| 0.89 | 2.80 | 0.521 |
| 0.90 | 2.80 | 0.523 |
| 1.00 | 2.78 | 0.543 |
| 1.50 | 2.64 | 0.763 |
| 2.00 | 2.41 | 0.851 |
| 2.50 | 2.23 | 0.870 |
| 3.00 | 2.09 | 0.878 |
| 3.10 | 2.06 | 0.880 |
| 3.50 | 1.95 | 0.862 |
| 4.00 | 1.84 | 0.808 |
| 5.00 | 1.73 | 0.712 |
| 6.00 | 1.70 | 0.646 |
| 7.00 | 1.70 | 0.628 |
| 8.00 | 1.71 | 0.656 |
| 9.00 | 1.70 | 0.713 |
| 10.00 | 1.66 | 0.795 |
| 11.00 | 1.60 | 0.891 |
| 12.00 | 1.49 | 0.972 |
| 13.00 | 1.35 | 1.030 |
| 13.60 | 1.24 | 1.045 |
| 14.00 | 1.16 | 1.030 |
| 15.00 | 1.03 | 0.959 |
| 17.50 | 0.830 | 0.772 |
| 20.00 | 0.736 | 0.596 |
| 21.80 | 0.711 | 0.473 |
| 22.50 | 0.717 | 0.433 |
| 25.00 | 0.734 | 0.323 |
| 27.50 | 0.764 | 0.242 |
| 30.00 | 0.791 | 0.197 |
| 35.00 | 0.833 | 0.144 |
| 40.00 | 0.855 | 0.102 |
| 45.00 | 0.878 | 0.0739 |
| 50.00 | 0.897 | 0.0549 |
| 55.00 | 0.911 | 0.0416 |
| 60.00 | 0.923 | 0.0310 |
| 62.00 | 0.927 | 0.0280 |

cally, $\Lambda(E)$ for arc-evaporated carbon was determined by use of Eqs. (16)–(19) in Ref. 16 and the data shown in Fig. 4. The values calculated by this method for Λ as a function of incident electron energy are shown in Fig. 5 by the long-dashed curve. Previously¹⁷ for arc-evaporated carbon we assumed that the experimental loss function, for $q \rightarrow 0$, could be represented by a single Drude-type function to obtain the needed parameters. Only small differences were found in the values of $\Lambda(E)$ obtained by the two methods of calculation. Figure 5 also shows published experimental values for electron attenuation lengths in carbon.^{10,18,19}

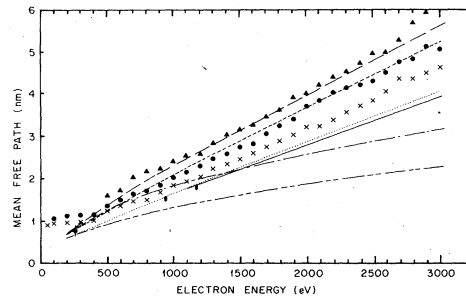


FIG. 5. Calculated values of inelastic mean free paths: long-dashed line, present study; solid line, Ref. 22, valence plus core electrons; short-dashed line, Ref. 20; long-dashed–short-dashed line, Ref. 23, for organics; dotted line, Ref. 22, valence electrons only; long-dashed–short-dashed–short-dashed–long-dashed line, Ref. 23, for elements. Also shown are experimental values of electron attenuation lengths: \times , \bullet , \blacktriangle , Ref. 10 for different film thicknesses of 8.1, 11.6, and 21.0 nm, respectively; \blacklozenge , Ref. 18; \bullet , Ref. 19.

Also shown on Fig. 5 are other calculations for $\Lambda(E)$ for arc-evaporated carbon. The short-dashed curve was obtained from a “universal curve” for solid organic insulators,^{20,21} assuming our measured density for arc-evaporated carbon of 1.90 g cm^{-3} . The universal curve was obtained from optical data that were available for six solid organic insulators in much the same way as the long-dashed curve was obtained for arc-evaporated carbon in the present study. In using this universal curve for solid organic insulators, we are treating amorphous carbon as the simplest organic material. In both the present calculations of $\Lambda(E)$ and the use of the universal curve for organics, actual optical properties were used and only valence electrons have been considered in the calculations. There is reasonable agreement between these calculated values of $\Lambda(E)$ and the measured values of $L(E)$. The agreement of the theoretical predictions for Λ from our universal curve for solid organic insulators with those based on the method of Ref. 16 is due to the similarity of the energy-loss function for carbon to the energy-loss functions found for organic materials.

Penn²² assumes in his calculations that the valence electrons can be modeled as a free-electron gas. Penn’s model thus does not take into account any deviations from free-electron gas behavior which are, however, taken into account by methods based on the measured optical properties of a material. The dotted curve in Fig. 5 is for the valence electrons only, while the solid curve includes both valence and core electron contributions to Λ . These calculations yield Λ values which are lower than our theoretical predictions but which still have an energy dependence similar to that of the experimental $L(E)$. As discussed in Ref. 10, our values would approach those of Penn as the width of the energy-loss function decreases. This illustrates the importance of using optical data in theoretical models to calculate $\Lambda(E)$.

The curves, in Fig. 5, calculated according to formulas given by Seah and Dench²³ do not show the energy variation found experimentally for carbon. If carbon is con-

sidered to be an organic material, then based on their formula for organics, their estimated values agree in magnitude with the experimental values for $E < 1000$ eV. However, the more natural formula to use for carbon would seem to be that for elements. In this case the formula by Seah and Dench gives estimates which are too low, as shown in Fig. 5.

It should be remembered that Λ and L are, in principle, different quantities. Λ is calculated for electrons in an infinitely thick medium, while the measured L value, at a given incident electron energy, may depend on the experimental conditions, including the thickness of the film. We plan to relate Λ and L through a Monte Carlo calculation which will take into account the experimental factors involved in the determination of L . It will then be possible to make a more direct comparison between calculated values of Λ and measured values of L .

IV. SUMMARY

We have presented the optical properties of arc-evaporated carbon films. We have then described briefly methods which can be used to calculate inelastic mean free paths for electrons with energies in the range of in-

terest for the interpretation of surface phenomena. These methods^{16,20,21} require a knowledge of the optical properties of the material over a range of photon energies which covers most of the oscillator strength of the valence electrons. In general, it is easier to obtain accurate values of the required optical properties than it is to measure the electron attenuation lengths in the energy region of interest. This theoretical approach, illustrated here for arc-evaporated carbon, can be used for any material for which the optical properties can be measured over essentially the whole energy range corresponding to the valence electron response.

ACKNOWLEDGMENTS

This research was sponsored jointly by the Solid State Sciences Division, Rome Air Development Center, under Interagency Agreement DOE No. 40-226-70, and the Office of Health and Environmental Research, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. One of us (S.M.D.) would like to thank the Oak Ridge Associated Universities for partial financial support.

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