# STRUCTURE ANALYSIS OF VACUUM EVAPORATED THIN CARBON FILMS

by

JOHN HOWARD KITTERMAN

B.S., Kansas State University, 1959

---

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1961

TABLE OF CONTENTS

# INTRODUCTION

Along with the X-ray diffraction technique, which is the principal method of studying atomic structure, electron diffraction has become increasingly important in the last two decades. As early as 1937, Z. G. Pinsker (12) had called attention to the possibility of using electron diffraction analysis for structure determination both independent of and cooperatively with the X-ray method.

X-rays are scattered by the electron clouds of atoms; accordingly, a treatment of X-ray synthesis results in the electron density distribution of the atoms in the sample. The scattering of electrons takes place when interaction occurs with the electric field produced by a combination of the atomic nuclei and the electron clouds. From the scattered intensity, it is possible to obtain the potential distribution of a crystalline lattice, of which the peaks correspond to the relative location of the centers of atoms. The difference in the nature of the interaction between X-rays and matter as compared to the interaction between electrons and matter brings about a difference in the absolute value of the scattering amplitudes for the two incident types of beams, as well as in the nature of the atomic scattering factor curves which depend on the atomic number and the value of $\frac{\sin \theta}{\lambda}$ ($\theta$ is the Bragg angle and $\lambda$ is the wavelength of the incident beam ) for both beams. The atomic scattering factor amplitudes of X-rays have a value of approximately $10^{-8}$cm (12). When referring to the intensities which are proportional to the square of the amplitudes, the electrons interact with the substance about a million times more strongly than do X-rays. Because of this greater interaction, the thickness of specimens in electron diffraction work is about 100 Å to 1000 Å, and the exposure time when producing electron diffraction patterns is of a few seconds as compared to hours in X-ray work. The method of electron diffraction is also well suited to the study of amorphous materials, especially carbon, because it is possible to observe the

electron diffraction intensity in the regions where it is very sensitive to variations in short inter-atomic distances (7).

In 1934 Warren (13) did some X-ray diffraction work on Commercial Carbon Black using an exposure time of some 20 hours. He was quick to point out that other workers had assumed carbon black as simply a fine-grained form of crystalline graphite from the three main halos on the diffraction pattern which corresponded to the (002), (100), and (110) lines of graphite. Since the appearance of the diffraction pattern was similar to a liquid or amorphous solid, it was deduced that one should try to gain more information from the diffraction patterns before making 'a priori' assumptions as to the crystallinity of the substance.

The method of Fourier integral analysis was used to obtain the atomic radial distribution about a given atom directly from the experimental scattering curve, without regard to whether the material was crystalline or amorphous. This technique was used together with the earlier radial distribution analysis set forth by Debye (3 ) in 1915. Warren's (13) conclusion that the experimental scattering curve could be satisfactorily interpreted on the basis of single graphite layers roughly parallel to one another is extremely interesting and should be a warning against not drawing hasty conclusions from a diffraction pattern which shows only three diffuse peaks.

More recent work by the X-ray diffraction method include that of Franklin (4 ), who in 1949 performed measurements on a carbon prepared by pryolysis of polyvinlidene chloride at 1000°C. It was pointed out that the degree of sharpening of bands in the diffraction pattern was a measure of the progress of the carbon toward graphite. Franklin (4) concluded that a comparison of experimental and calculated intensity curves indicated that 65 per cent of the carbon was in the form of highly perfect and planar graphite-like layers of diameter 16±1 Å, and 35 per cent was in a highly disordered state. About 55 per cent of

the graphite-like layers were grouped in pairs of parallel layers with an interlayer spacing of 3.7 Å, and 45 per cent of the layers showed no mutual orientation. Further, the graphite-like layers were contained in small groups of particles having a mean separation of 26 Å. The exact nature and shape of the particles could not be determined from the radial distribution curve. However, only about two-thirds of the total carbon was involved in graphite-like layers of diameter 15-20 Å. The remaining one-third of the less highly organized structure was presumably distributed around the edge of the layers. It seemed that each particle contained only a very small number of layers, possibly only one parallel layer per group. It should also be pointed out that, except for the diffuse (002) line, all other intensity maxima could be related to (hk0) reflections of graphite. Higher orders of (002) were not observed, nor were there any (hkl) (hh0) reflections. Hence, it may be inferred that such carbon contains graphite layers which are well ordered in two dimensions, but show little tendency to parallel stacking and no three dimensional crystalline order.

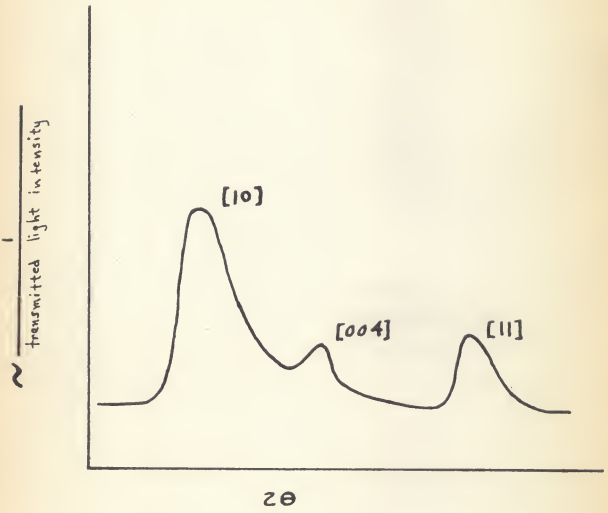
In an earlier paper by Warren (14) on X-ray diffraction in random layered lattices, it was stated that an amorphous material like carbon exhibits crystalline (00l) and two dimensional diffuse (hk) reflections. In the paper the preceding reflections are discussed along with a diagram from a photometer trace in which the symmetry of the (004) line is evident as compared to the unsymmetrically displaced and broadened peaks for (10) and (11)lines (See Plate I.)(14). This effect has been observed by a number of investigators.

Upon heating "non-graphitic" (only (hk) and (00l) reflections present) carbons between the temperatures of 1700°C and 3000°C Franklin (5), in 1951, observed a continuous and homogeneous evolution from a non-graphitic to a graphitic structure. These were designated as "graphitizing carbons". Other non-graphitic carbons, the "non-graphitizing carbons", showed no trace of homogeneous development

EXPLANATION OF PLATE I

Microphotometer record of the diffraction pattern of a heat-treated carbon black, showing two dimensional lattice reflections. Radiation used was CuK$\alpha$= 1.539 Å monochromated by reflection from rock salt.

PLATE I



even after heating to 3000°C for many hours.

It seemed clear that the interlayer spacing in the graphitic carbons must be directly related to the degree of mutual orientation of the layers. It should be noted that after heat treatment among the carbons, labeled as graphitizing, inter-layer spacing ranged from 3.36 Å to 3.43 Å, whereas after heat treatment the non-graphitizing interlayer spacings were 3.44-3.45 Å. It is interesting to note that an example of a non-graphitic graphitizing carbon before heat treatment had only the (100), (004), and (110) lines present. After heat treatment the following lines were present: (002), (100), (101), (102), (004), (103), (110), (112), (006), (200), (201), and (114).

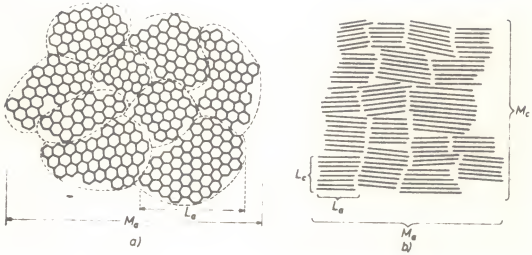
Measurements of the width of the (002) and (004) lines showed that there was a mixture of at least two inter-layer spacings in the graphitic carbons. The (004) line was always considerably broader (in reciprocal space) than the (002) line, whereas if the interlayer spacing were constant in a given carbon, all (00 $\ell$) lines should be the same small breadth. One is led, therefore, to suppose that the graphitic carbons contain a mixture of oriented and disoriented layers, the spacing of the disoriented layers being greater than the spacing of the oriented layers. In the non-graphitizing carbons the interlayer spacing was constant at 3.44 Å, and in the graphitic carbons the apparent interlayer spacing decreases with increasing graphitization. In all graphitic carbons, whatever the degree of graphitization, the small groups of oriented and disoriented layers within the parallel packet retain certain of the structural characteristics of crystalline graphite and the non-graphitic carbons.

More recent papers by Steward and Cook (11) and Bacon (1) confirm the general description of layering as concluded by Franklin (5). Upon the defining of the parameters $L_a$, $L_c$, $M_a$, $M_c$, the following diagram (Plate II) (11) will illustrate the structure of "turbostatic" packing. This type of packing gives symmetrical

EXPLANATION OF PLATE II

Diagrammatic representation of mosaic parameters $M_a$, $M_c$ in relation to $L_a$, $L_c$. (a) plane view of oriented macro-unit (b) elevation of oriented macro-unit

PLATE II



(00$\ell$) reflections, but two dimensional unsymmetric (hk) lines which modulate into normal (hk$\ell$) reflections when ordering occurs.

$L_a$ is the average overall dimension of the crystallites measured parallel to layer planes.

$L_c$ is similar to $L_a$, but perpendicular to layer planes.

$M_a$ is the size of the layer over which there is reasonable continuity and regularity of atomic arrangement though less perfect than in the area of size $L_a$ as measured by X-ray diffraction.

$M_c$ is similar to $M_a$, but referring to a mosaic macro-unit of stacked parallel layer groups.

Evaporation of carbon onto a substrate in a vacuum differs from carbons analyzed previously in that, ideally, only carbon atoms are involved as opposed to carbon with impurities, for example those studied by Franklin (5). A recent work (11) on cellulose, for example, has shown that contamination by silica can lead to very extensive graphitization.

Palin (10) reported that "macrocrystalline" carbon with an interlayer spacing of 3.45 Å has been prepared by the sublimation of artificial graphite under high vacuum. The carbon is greater than 99 per cent pure with an ash less than 0.4 per cent. The carbon planes of individual crystallites lie approximately parallel to the surface on which deposition occurs (surface was not mentioned), and the crystalline size, as shown by the sharpness of the lines in the diffraction pattern, was similar to that of artificial graphite. Lines present were (002), (100), (004), and (110).

Contrary to Palin's expectations the material did not graphitize easily. Temperatures in the range 2800°C to 3000°C were needed to convert a sample into graphite. It was suggested that due to the stability of the carbon some sort of "cross-linking" between carbon layers was occurring.

Recently, the Japanese workers Kakinoki, Katada, Hanawa and Ino(7) published two papers on the study of evaporated carbon films by means of electron

diffraction techniques. Most of the previous material has been concerned with the X-ray studies of amorphous-like carbons. The resulting carbon structure was called an aggregrate of small graphite-like particles. However, different results were obtained from electron diffraction than from X-ray diffraction.

The films used were vacuum evaporated at room temperature at a pressure of $10^{-4}$mm of mercury with glass microscope slides as substrates. Film thicknesses were about 100 Å. The films were thin enough so that the multiple scattering of electrons was not considered as appreciable.

The electron diffraction plates, which rotated rapidly about the center of the pattern, were microphotometered, and the photographic densities were converted into intensities of electrons by the Karle and Karle (9) method.

Applying the Fourier radial distribution type of analysis similar to that for free molecules, it was found that the first nearest neighbor to a given carbon atom resided at a distance of 1.50 Å, compared to the first nearest neighbor distances at approximately 1.42 Å and 1.55 Å for graphite and diamond, respectively, These values indicated, perhaps, a graphite-like and diamond-like superposition effect. Both the radial distribution and correlation methods of analysis were used.

Electron diffraction intensity curves were constructed with the assumption that diamond-like bonds were present, and they matched the observed intensity up to approximately s=20 $Å^{-1}$ ($s=\frac{4\pi \sin \theta}{\lambda}$). However, an important phase shift between the calculated curve and observed curve appeared beyond s=24 $Å^{-1}$. It was suggested that there should be two or more kinds of bond distances instead of a single kind of 1.5 Å.

These workers were quick to point out that if no intensity data were known beyond s=18 $Å^{-1}$, which is the largest value of s observed by MoK$\alpha$ radiation ($\lambda$ = 0.71 Å), and because of the damping nature of the atomic scattering factor for X-rays, it could not be decided easily whether the C-C bonding is a single kind of 1.50 Å or of two kinds at 1.42 Å and 1.55 Å.

It was proposed that the small individual diamond and graphite regions would be as small as several Angstrom units and have no mutual orientation, which is similar to Plate II indicated previously in relation to the random orientation of graphite in a given two-dimensional layer. A two-dimensional model was deduced by the Japanese workers (7) regarding the structure of the film (See Plate III) (7). They further constructed a probable model of the graphite-diamond arrangement as a three-dimensional random network similar to glass. The model was consistent with the observed density of the film which is between that of diamond and graphite. The number of diamond-like distances was somewhat larger than the graphite-like distances. These factors account for the high mechanical strength of evaporated carbon films.

In films prepared by vacuum evaporation the carbon film is formed by the recombination of carbon atoms. Since it does not depend on the starting material, the differences in the structures of carbons deduced from X-ray and electron diffraction work might be expected; however, the X-ray work of Palin (10) was with vacuum evaporated films and his analysis only verified the structure of previous carbons as analyzed by X-ray methods.

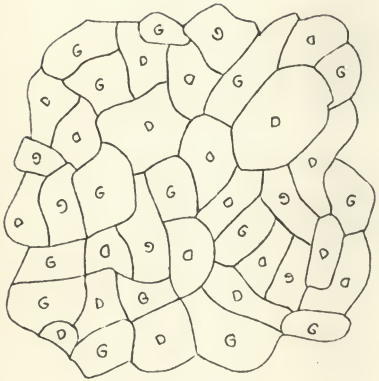
The structure analysis of films deposited at room temperature and then heated to higher temperatures was done in 1960 by Kakinoki, Katada, and Hanawa (8). The film temperature was indicated by a thermocouple placed near the specimen. The highest temperatures obtained in each treatment were 500°, 700°, 900°, 1000°, and 1200°C. Each specimen was kept at the highest temperature for 1 minute, and then allowed to cool to room temperature, the rate of temperature decrease being very rapid.

Electron diffraction diagrams show a gradual change in the structure with increase of the temperature in the heat treatment. At 1200°C, the diffraction patterns change into sharp rings with asymmetric line profiles, and are all indexed

EXPLANATION OF PLATE III

Two-dimensional representation of arrangement of the graphite-like and diamond-like regions.

PLATE III



with the (hk0) of graphite having a lattice constant of a= 2.456 Å. No (hkℓ) ( ℓ≠ 0) lines could be observed. When the incident beam was normal to the surface of the film the (002) and (004) did not appear, but by rocking the sample so that the beam was inclined to the surface the (002) and (004) lines did appear. The interlayer spacing was estimated to be 3.41 Å. From these observations, it is evident that the films heated to higher temperatures exhibit random layer structure with each layer parallel to the film surface. This is similar to the graphitic carbons mentioned earlier in connection with X-ray analysis.

In this review it is seen that the structures exhibited by bulk carbon and evaporated films of carbon are quite similar. No previous work was done, though, with a substrate except for the glass microscope slides. It might be possible that the amorphous nature of the glass substrate caused the amorphous carbon formation. The intriguing possibilities of using a substrate containing diamond-like bonding, while forming the films at different temperatures, has resulted in this thesis. Hence, this thesis will involve the investigation of the crystalline-like structure of thin carbon films deposited in vacuum on a temperature-controlled and oriented substrate, silicon, which exhibits diamond-like bonds, and will seek to determine if the C-C bond distances of these thin films are predominantly graphite-like, diamond-like, or perhaps a combination of both.

## APPARATUS AND EXPERIMENTAL PROCEDURE

The heat source for the formation of the thin carbon films analyzed in this thesis was a furnace made of monel metal ( 60% Ni, 33% Cu, 6.5% Fe by weight) (See Plate IV). Monel metal has a high melting point and a low specific heat, making it quite suitable as a furnace material. A block of

EXPLANATION OF PLATE IV

Fig. 1 Side view of furnace

Fig. 2 Top view of furnace

A. Carbon film source: spectroscopic graphite rod 1mm in diameter

B. Carbon film

C. Silicon crystal substrate

D. Silver chloride

E. Copper sheet

F. Thermocouple junction

G. Monel block: 3 in. long and 0.6 in. in diameter

H. 44 turns of Nichrome wire, resistance 1.613 ohms per foot

I. Asbestos jacket

J. lavite table

PLATE IV

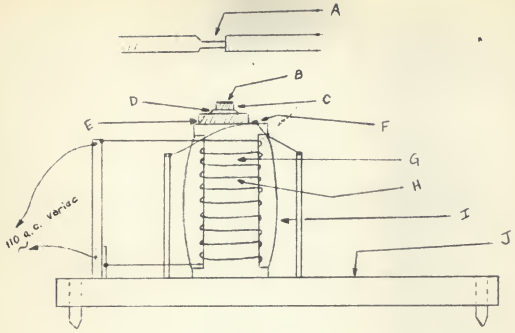



Fig. 1

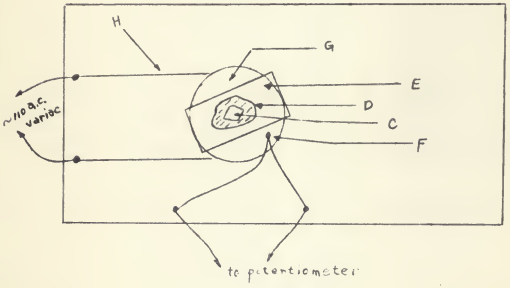



Fig. 2

monel was machined on a lathe into the form of a cylindrical spool, which was wound with Nichrome wire with sheet mica interspacing. The furnace was designed to reach temperatures in excess of 600°C.

The temperature of the silicon substrate, subsequently placed upon the top of the furnace, was measured by means of a Chromel-Alumel thermocouple which was silver-soldered to the top of the furnace. The generated emf was read on a Rubicon potentiometer. It was also necessary to cover the cylindrical sides of the furnace and windings with a coat of asbestos in order to maintain heat conduction to the monel block and sample under evacuated conditions. The electrical power and thermocouple leads were introduced into the vacuum chamber through vacuum seals. The power to the furnace was controlled by a 9 amp variac, the primary voltage being regular line 110 volt a.c.

A thin wafer of a single silicon crystal ( diamond, face centered cubic) was used as a substrate for the evaporated films. The crystalline wafer ($\sim$1 mm thick and surface area $\sim$1 sq. cm ) was cut perpendicular to the [111] crystallographic direction as verified by back-reflection Laue photographs. By presenting a diamond-like lattice to the recombining carbon atoms, it was hoped that the carbon atoms might take up the diamond structure. The silicon crystal was next polished with silicon carbide paper and with varying grades of emery abrasive ( 55-75% aluminum oxide, balance is iron oxide (magnetite) ) powders ending with 0.5 micron aluminum oxide powder. After polishing, the crystal was etched in a boiling solution of ten per cent sodium hydroxide for two minutes. The etched wafer was then washed with distilled water.

Difficulties arose in establishing a thermal contact between the furnace top and the silicon crystal in a vacuum. Thermal contact was finally established by first silver-soldering a small copper sheet to the top of the

furnace. The silicon wafer was then joined to the copper sheet by melting a speck of silver chloride on the copper and placing the silicon wafer on the liquid droplet of silver chloride. The advantage of the silver chloride as a thermal binding medium was that silver chloride readily stuck to the copper and silicon, yet permitted the easy removal of the silicon crystal from the furnace top without breaking the brittle silicon wafer and its carbon film coating. After the solidification of the silver chloride, the silicon crystal was masked and a film of gold was vacuum-evaporated over the furnace top to prevent silver chloride contamination of the surface of the silicon crystal at elevated temperatures.

Cylindrical rods of "spectroscopic graphite" 3 mm in diameter were used as electrodes. The end of one of the graphite rods was cut into the shape of a cylinder 1 mm in diameter and 3 mm long. This constricted region then served as the source of carbon atoms for the films to be evaporated. (See Plate IV). The two rods of graphite were then pressed together and heated to a sufficient temperature for evaporation in a vacuum of approximately 0.6 microns, similar to the method of Bradley (2). A thin film of carbon approximately 500 Å thick was then deposited onto the surface of the temperature controlled substrate. The silicon substrate was established at an equilibrium temperature before evaporation. At temperatures above 500°C, the visual color of the furnace top and the silicon crystal was the same to the naked eye, indicating a good thermal contact. The evaporated carbon film ( one film for each of the temperatures 31°, 202°, 403°, and 595°C) was loosened from the substrate by submerging the silicon crystal into hot (not boiling) ten per cent sodium hydroxide. The loosened film was then floated onto the surface of distilled water where it was picked up on a 200 mesh stainless steel microscope grid. The film was then ready for electron diffraction analysis.

## EXPERIMENTAL ANALYSIS

The electron diffraction work for this thesis was done with an R.C.A. E.M.U.-2D electron microscope with a selected area diffraction attachment.

All diffraction plates were exposed for ten seconds; all were developed for the same time at the same temperature. The calibration of the distances on the plates was done with magnesium oxide. Two separate sets of electron diffraction patterns were made on each sample. The first run for each carbon film prepared at the substrate temperatures 31°, 202°, 403°, and 595°C, contained three diffraction patterns plus a step blackening exposure. A second series of diffraction patterns from films prepared at all four temperatures plus a step blackening set of exposures was done on one plate.

The accurate measurement of the electron intensity, I , of a diffraction pattern is measured by the amount of blackening the electron intensity causes on a photographic plate. The photographic blackening (or density),B, is in turn measured on a densitometer by the amount of visible light the plate will transmit and is defined by $B=\log_{10}T_o/T$ where $T_o$ is the intensity of the light beam transmitted through an unexposed portion of the plate and T is the light intensity transmitted through an exposed portion of the plate. For the step blackening calibration the exposure, E=It, is varied by keeping the electron intensity constant and varying the time,t, of the exposure. The resulting plot of B versus E (for ideal film characteristics B would be directly proportional to I) is corrected for deviation from linearity by fitting a fourth power curve to the experimental B versus E curve, where B versus E is linear for small E. In this way a quantity proportional to the experimental electron intensity is obtained from the blackening curve.

The electron diffraction plates were then densitometered on a Leeds and Northrup machine. The densitometer trace for each temperature consisted of the

blackening, B , versus s plus a step blackening plot of B versus E for correcting the deviation of the blackening curve from linearity so that B is directly proportional to the scattered electron intensity, I.

The data taken from the densitometer traces were set up for analysis on the IBM-650 computer. Values of B were taken for incremental values of $s = 0.091\ \text{Å}^{-1}$. Approximately sixty points were used for representing the diffraction from each carbon film at the four temperatures.

In order to be able to plot the radial distribution of atoms versus distance of other atoms from a given reference atom the method of radial distribution analysis was used (7); the foundation of this method goes back to Debye's theory of scattering from amorphous and non-crystalline arrays of atoms. The intensity scattered by a non-crystalline array of atoms is

$$I = \sum_m \sum_n f_m f_n \ (\sin sr_{mn}/sr_{mn}) \tag{1}$$

where $f_m$ and $f_n$ are the atomic scattering factors for the $m^{th}$ and $n^{th}$ atoms, and $r_{mn}$ is the magnitude of the vector separating the two atoms. For our case there is only one kind of atom and (1) becomes

$$I = Nf^2 + f^2 \sum_m \sum_{m \neq n} ( \sin sr_{mn}/sr_{mn} ) \tag{2}$$

where N is the total number of atoms in the path of the electron beam. By applying the Fourier integral theorem and inverting the experimental intensity function one can obtain the radial distribution function of the specimen without assuming its final structure.

In performing the summation (2) each atom in turn becomes the reference atom, and there will be N terms due to the interaction of each atom with itself. Thus the value of each of these terms will become unity since as $r_{mn} \rightarrow 0$, $( \sin sr_{mn}/ sr_{mn} ) \rightarrow 1$.

Equation (2) becomes

$$I = Nf^2 \ ( 1 + \sum_{m \neq n} \sin sr_m / sr_m \ ) \tag{3}$$

Assuming the distribution of atoms about any reference atom may be regarded as continuous, the summation is replaced by an integral

(4) $$I = Nf^2 \left[1 + \int_0^\infty 4\pi r^2 \rho(r) (\sin sr/sr)\, dr\right]$$

where $\rho(r)$ is the radial atomic distribution function, i.e. the number of atoms per unit volume between r and r+dr, and $4\pi r^2 \rho(r) dr$ is the number of atoms in a spherical shell of radius r and thickness dr. Let $\rho_o$ be the average density of atoms; d the mass density of the specimen; m the mass of the sample scattering electrons; M the atomic weight; $N_o$ Avagodro's number; V the effective volume of the specimen scattering electrons and N the total number of atoms in the effective volume V. Then

$$d = m/V = MN/VN_o \quad \text{and} \quad V = MN/N_o d \quad \text{where } \rho_o = N/V$$

so that $\rho_o = N_o d/M$ ( this allows d to be calculated from $\rho_o$ and compared to the d of the sample)

Let us add and subtract $Nf^2 \int_0^\infty 4\pi r^2 \rho_o (\sin sr/sr)\, dr$ from (4),

(5) $$I = Nf^2 \left[1 + \int_0^\infty 4\pi r^2 (\rho(r) - \rho_o)(\sin sr/sr)\, dr + \int_0^\infty 4\pi r^2 \rho_o (\sin sr/sr)\, dr\right]$$

The second integral is zero except for very small s, where the scattered intensity cannot be resolved from the main beam and is unobservable.

So (5) becomes

(6) $$I/Nf^2 - 1 = \int_0^\infty 4\pi r^2 (\rho(r) - \rho_o)\, (\sin sr/sr)\, dr$$

By means of the Fourier integral theorem

(7a) $$r\,(\rho(r) - \rho_o) = 2/\pi\, (1/4\pi) \int_0^\infty s\, i(s) \sin sr\, ds$$

where

$$i(s) = \frac{I - Nf^2}{Nf^2}$$ and is the

$$\frac{\text{experimental intensity - background intensity}}{\text{background intensity}}$$ then

(7b) $$4\pi r \Delta(r) = 2/\pi \int_0^\infty s\, i(s) \sin sr\, ds$$
(where $\Delta(r) = \rho(r) - \rho_0$)

Since the integral on the right is to be evaluated by reverting to a series which will be terminated after a finite number of terms, a damping factor in the form of a Gaussian function is inserted (7), and

(8) $$4\pi r \Delta^*(r) = 2/\pi \int_0^{s_0} s \exp(-as^2)\, i(s) \sin sr\, ds$$
(where a= 0.00373)

Then

(9) $$\frac{4\pi r \Delta^*(r)}{k} = \sum_n s_n \exp(-as^2)\, i(s) \sin s_n r$$
(where $k = 2/\pi \Delta s$)

In this present problem the sum on the right consists of approximately sixty terms. Although $4\pi r \Delta^*(r)$ differs from $4\pi r \Delta(r)$, the positions of the peaks in $4\pi r \Delta(r)$ versus r, which correspond to the centers of atoms, are essentially unchanged by the damping factor. The damping factor's purpose is to remove the extraneous ripples from the $4\pi r \Delta(r)$ versus r curve due to series termination.

It is recalled that

$$i(s) \text{ is proportional to } \frac{I(s) - Nf^2}{Nf^2} \quad \text{where}$$

I(s) is the experimental scattering intensity and i(s) is the reduced intensity. Since the total independent scattering $Nf^2$ for electron diffraction is not known accurately, a background curve, I'(s), was constructed from each of the experimental scattering curves by a moving average technique (6),

$$I'(s) = 1/a' \int_{s-a'/2}^{s+a'/2} I(s')\, ds' \quad (a' = 18\ \Delta s \text{ increments})$$

where the background curve, I', was started 8 $\Delta s$ increments back from the first peak in each of the experimental scattering curves for the four temperatures 31°, 202°, 403°, and 595°C.

All of the preceding operations were done by the IBM-650. A program corrected the non-linearity of B versus E and constructed a reduced scattering curve from the data. It then performed the previously indicated summations to get $\frac{4\pi r \alpha(r)}{k}$ versus r, the peaks of which correspond to the positions of neighboring carbon atoms with respect to any arbitrary carbon atom taken as an origin.

## RESULTS

The densitometer traces of the carbon films evaporated at 31°, 202°, and 403° exhibit only two diffuse peaks at approximately 3.1 $Å^{-1}$ and 5.8 $Å^{-1}$. The film deposited at 595°C exhibits three peaks at approximately 1.8 $Å^{-1}$, 3.1 $Å^{-1}$, and 5.8 $Å^{-1}$ (See Plate V). The only effect of temperature on the carbon films appears to be the gradual sharpening of the peaks in the densitometer traces of B versus s. The difference between the sharpness of the peaks in the 31° curve and the peaks in the 595° curve is very marked (See Plate V). No consistant shifting of peaks with increased temperature was observed. The s values of the experimental peaks can be compared with the s values for the (002), (100), and (110)-(200) lines of graphite.

The plots of the radial distribution of carbon atoms versus distance from a given carbon atom as an origin, r, exhibit two peaks. The first peak lies at an average distance of 1.41 Å; the second peak lies at 2.51 Å (See Plate VI).

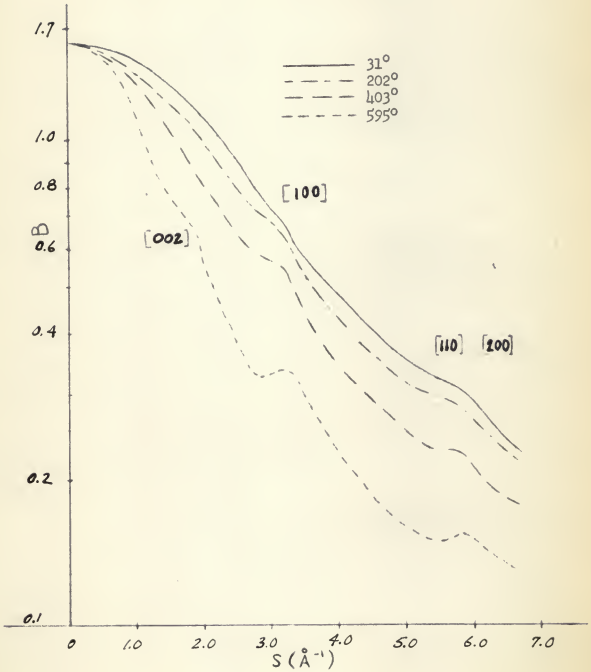
## DISCUSSION

The first peak in the radial distribution curve at 1.41 Å indicates that the first nearest neighbor distance to a given carbon atom is nearly the graphite first nearest neighbor distance at 1.42 Å. The second experimental

EXPLANATION OF PLATE V

Densitometer traces of blackening of an electron diffraction pattern versus s for the four carbon films formed at temperatures 31°, 202°, 403°, and 595°C.

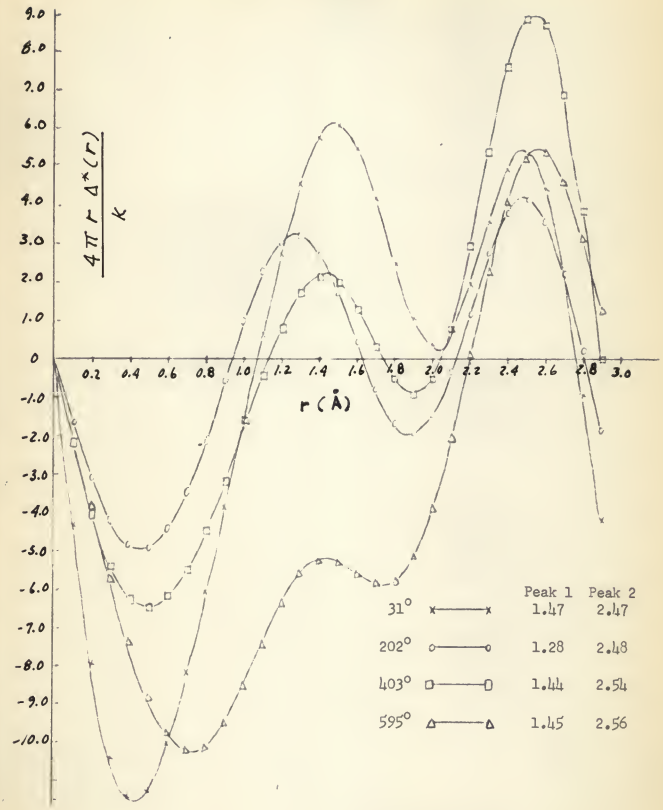
PLATE V


1.7
1.0
0.8
0.6
0.4
0.2
0.1
B
31°
202°
403°
595°
[100]
[002]
[110]
[200]
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
S (Å⁻¹)

EXPLANATION OF PLATE VI

Experimental curves of the radial distribution function versus r for the four carbon films formed at temperatures of 31°, 202°, 403°, and 595°C.

PLATE VI


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
$\frac{4\pi r \Delta^x(r)}{k}$
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0
r (Å)
Peak 1 Peak 2
31° 1.47 2.47
202° 1.28 2.48
403° 1.44 2.54
595° 1.45 2.56

peak at 2.51 Å falls well above the second nearest neighbor distance of graphite at 2.45 Å and close to the second nearest neighbor distance of diamond at 2.54 Å. The first, second, and third nearest neighbor distances of graphite are 1.42 Å, 2.45 Å, and 2.83 Å, respectively. The first, second and third nearest neighbor distances of diamond are 1.55 Å, 2.54 Å, and 2.98 Å, respectively. From these values, one can see that a possible explanation of only one peak falling above the second and below the third nearest neighbor distance of graphite could be the lack of resolution of two single peaks in such close proximity as 2.45 Å and 2.83 Å. The resulting experimental peak falling above 2.45 Å could then be interpreted as the overlapping of the radial distributions of the graphite second and third nearest neighbors.

The Japanese workers (7) interpreted their second experimental peak at 2.55 Å as the overlapping of the radial distributions of the second and third nearest neighbor atoms of graphite and diamond. They were able to show that by including both diamond and graphite second and third nearest neighbors, there resulted a calculated peak value of the radial distribution curve very close to 2.55 Å. The first experimental peak in the Japanese (7) paper was at approximately 1.50 Å, midway between the first nearest neighbor distance of graphite at 1.42 Å, and diamond at 1.55 Å. Since the number of first nearest neighbors in graphite and diamond is the same, they were able to show that the overlapping of a calculated radial distribution curve consisting of a mixture of graphite and diamond gave a first nearest neighbor at approximately 1.50 Å.

One immediately sees from the positions of the author's peaks, the first below that of graphite or diamond and the second above graphite, that analysis similar to that of the Japanese workers will perhaps satisfy the problem for the second peak. The first peak, however, remains slightly below the graphite

first nearest neighbor distance, and definetly below the diamond first nearest neighbor distance.

The average distance of the graphite second and third nearest neighbors is approximately 2.60 Å. An overlapping of the radial distribution peaks of graphite second and third nearest neighbors would then shift the experimental radial distribution peak to a value of approximately 2.60 Å. This peak would be closer to the graphite second nearest neighbor peak at 2.45 Å than the graphite third nearest neighbor peak at 2.83 Å because there are twice as many graphite second nearest neighbor atoms as there are graphite third nearest neighbor atoms. The author's experimental values of 1.41 Å and 2.51 Å are then about 0.01 Å and 0.09 Å below the values 1.42 A and 2.60 A, respectively. The values of 1.42 Å and 2.60 Å were gotten by considering only graphite-like bonds being present. The first peak at 1.42 Å was resolved in the analysis. The 2.45 Å and 2.83 Å peaks were not individually resolved, but overlapping gave a single peak at approximately 2.60 Å.

Rapid rotation of the electron photographic plates about the center of the plate, as done by other workers (7)(9), was not possible in the author's analysis. Therefore grain irregularity in the emulsion of the plates could have affected slightly the positions of the peaks of the radial distribution curve. Another possible source of error could have been in the background intensity calculation. The background intensity depends mainly on $Nf^2$, but f is not known accurately for electron diffraction work, hence the necessity for construction of a background intensity curve from the experimental intensity curve. The positions of the peaks in the radial distribution curve depend slightly on where one starts on the experimental intensity curve in calculating the background by the sliding average method.

## CONCLUSION

Evidently, a diamond-like substrate did not affect the recombining carbon atoms. The films exhibited the characteristic two-dimensional graphite-like structure by the absence of (hk$\ell$) halos and the apparent presence of graphite-like bond distances. Random layering is present so that the model of Franklin and others (See Plate II) appears to be correct for the thin films analyzed.

It should be pointed out that had the first peak on the radial distribution curve fallen between the first nearest neighbor distance of graphite and diamond it would have been necessary to follow the analysis methods similar to those of the Japanese workers (7). It would have been necessary to look at the experimental intensity curve for values of $s > 24$ $\text{Å}^{-1}$. Then by assuming only a single bond-type of approximately 1.50 Å for the first nearest neighbors and a single bond-type of approximately 2.55 Å for the second nearest neighbors, an intensity curve could be calculated. As the Japanese workers (7) showed, this calculated curve has a phase shift beyond $s=24$ $\text{Å}^{-1}$ with respect to the experimental intensity curve. This important fact led them to consider the two bond types: graphite-like and diamond-like. Using both graphite-like and diamond-like bond distances for first and second nearest neighbors, also for first, second and third nearest neighbors, they constructed two more intensity curves. These resulting calculated curves were both in phase with the experimental curve for all s values visible. Hence their conclusion was that the thin films were a mixture of graphite-like and diamond-like carbon bonds.

However, it is the opinion of the author that the present films do not exhibit diamond-like bonding. No amount of graphite-like and diamond-like bonding would shift the first nearest neighbor peak of the radial distribution curve to a position approximately equal to that of only graphite.

It is possible that the films analyzed in this thesis were too thick. It might be that only films of the order of 300 Å or less exhibit graphite-like and diamond-like bonding. For further study such films could be deposited at various temperatures still using a diamond-like substrate. Then the results could be compared with that of films deposited at room temperature on various substrates and subjected to heat treatment. This effort would lead to more conclusive results on the existence of diamond-like bonds in thin carbon films.

ACKNOWLEDGMENT

The author wishes to express his thanks for the time and assistance given him by Dr. R. D. Dragsdorf. Thanks go also to L. W. Phillips for assistance in construction of part of the apparatus used in this thesis, and to the author's wife, Dee, for many hours of typing necessary for the preparation of this thesis.

REFERENCES

(1) Bacon, G.E.
The Interlayer Spacing of Graphite, Acta Cryst.,Nov.,1951, 4: 558-561

(2) Bradley, D.E.
Evaporation of Thin C Films for use in Electron Microscopy,
Brit. Jour. Appl. Phys., Feb., 1954, 5: 65-66

(3) Debye, P.
Zerstreuun von Rontgenstrahlen, Annal. der Physik,
Feb., 1915, 46:809-823

(4) Franklin, R.E.
The Interpretation of Diffuse X-ray Diagrams of C,
Acta Cryst., Mar., 1950, 3: 107-121

(5) Franklin, R.E.
The Structure of Graphitic Carbons, Acta Cryst., May, 1951, 4: 253-261

(6) Kac,M., Uhlenbeck, G.E., Hibbs, A.R., Van Der Pohl, B.,
Probability And Related Topics In Physical Sciences, 1959,
Pages 223-224, Interscience Publishers, Ltd.

(7) Kakinoki, J., Katada, K., Hanawa, T., and Ino, T.
Electron Diffraction Study of Evaporated Carbon Films
Acta Cryst., Mar., 1960, 13: 171-179

(8) Kakinoki, J., Katada, K. Hanawa, T., Heat Treatment of Evaporated Carbon
Films, Acta Cryst.,May, 1960, 13: 448-449

(9) Karle, J., and Karle, I.L.
Internal Motion and Molecular Structure Studies, J. Chem. Phys., Nov.,
1949, 17: 1051-1058

Internal Motion and Molecular Structure Studies by Electron Diffraction II.,
J. Chem. Phys., July, 1950, 18: 957-962

(10) Palin, D.E.
Macrocrystalline Carbon, Nature, Oct., 1956, 178: 809-810

(11) Steward, E.G., and Cook, B. P.
Graphitization in Oriented Carbons, Zeit. fur Krist., Oct, 1960,
114: 245-260

(12) Vajnstejn, B.K.
Structure Analysis By Electron Diffraction, Nuovo Cimento Suppl.,
Sep., 1956, 3: 773-797

(13) Warren, B.E.
X-ray Diffraction Study of Carbon Black, J. Chem. Phys., Sep., 1934, 2: 551-555

(14) Warren, B.E.
X-ray Diffraction in Random Layered Lattices, Phys. Rev., May, 1941, 59: 693-698

# STRUCTURE ANALYSIS OF VACUUM EVAPORATED THIN CARBON FILMS

by

JOHN HOWARD KITTERMAN

B.S., Kansas State University, 1959

---

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1961

X-ray analysis is the primary tool for the structure analysis of matter. However, another tool, electron diffraction, has become very important in the last decade. Electron diffraction methods are particularly suited to the analysis of thin films, because it is possible to observe the scattered electron intensity in regions where it is very sensitive to short interatomic distances.

X-ray analysis has been used by many workers to determine the structure of amorphous carbons. The results are that the amorphous carbon can be described as randomly oriented two-dimensional layered structures with practically no three-dimensional ordering. Scattered intensity versus scattering angle for the bulk carbons showed diffuse halos corresponding to the (hk0) reflections of graphite along with (002) and (004) reflections. (hk$\ell$) reflections were entirely absent.

Electron diffraction analysis on thin carbon films has been done recently. Thin films of carbon are vacuum evaporated onto glass microscope slides as substrates. The resulting carbon film structure has been interpreted as consisting of a mixture of approximately 50 per cent graphite-like and 50 per cent diamond-like bonds with a three-dimensional structure similar to glass. As in X-ray analysis, only (hk0), (002) and (004) reflections appeared confirming the lack of three-dimensional ordering. Heat treatment of vacuum evaporated films analyzed by electron diffraction methods showed the gradual transformation of the diffuse (hk) and (00$\ell$) halos into sharp diffraction lines.

The work in this thesis will be concerned with the structure determination of vacuum evaporated thin carbon films deposited onto a temperature controlled diamond-like substrate, silicon. It might be possible that the diamond-like substrate would affect the recombining carbon atoms by epitaxial growth.

A furnace in the shape of a cylindrical spool was made of monel metal. The spool was wound with Nichrome wire with sheet mica interspacing. It was necessary to add a jacket of asbestos to maintain conduction under vacuum conditions. The single crystal substrate, silicon, was then polished with varying grades of emery

and aluminum oxide powders and etched with a 10 per cent solution of boiling sodium hydroxide for two minutes. Thin carbon films approximately 500 Å thick were then vacuum deposited on the silicon substrate for the temperatures 31°, 202°, 403°, and 595°C. Temperatures were measured by a Chromel-Alumel thermocouple. The changes of the carbon films associated with temperature effects appeared in the gradual sharpening of the diffraction halos in the electron diffraction plates. This sharpening can be interpreted as progress toward crystallization of the evaporated carbon films.

Electron diffraction patterns of the carbon films were analyzed by the radial distribution method. Peaks in the radial distribution curve versus r (the distance from a given carbon atom as an origin) were found at 1.41 Å and 2.51 Å. This indicates that the first nearest neighbor distance of a carbon atom is approximately 1.41 Å; an overlapping of the radial distribution function of the second and third nearest neighbors at 2.45 Å and 2.83 Å gives a peak at approximately 2.51 Å. These values compare with the published values of 1.42 Å and 2.60 Å. It was concluded that the structure of the thin carbon films analyzed in this thesis could be explained by only graphite-like bond distances. The two-dimensional randomly oriented structure, as found by X-ray methods, seemed to fit also for the films analyzed in this thesis.

It was suggested that further study on thinner carbon films of the order of 300 Å or less could possibly verify the diamond-like structure found in thin carbon films by other workers.