Dense "diamond-like" hydrocarbon films grown at the NASA Lewis Research Center by radio frequency self bias discharge and by direct ion beam deposition were studied. A new method for categorizing hydrocarbons based on their atomic number density and elemental composition was developed and applied to the "diamond-like" hydrocarbon films. It was shown that the "diamond-like" hydrocarbon films are an entirely new class of hydrocarbons with atom number densities lying between those of single crystal diamond and the adamantanes. In addition, a major review article on these new materials was completed in cooperation with NASA Lewis Research Center personnel.
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6. APPENDIX, "EMPIRICAL CATEGORIZATION AND NAMING OF
   'DIAMOND-LIKE' CARBON FILMS" ............................. 5
1. INTRODUCTION

The research was directed towards understanding the relationship of the properties of the dense "diamond-like" hydrocarbon films to the structure and composition of the films. All of the films studied were grown at the NASA Lewis Research Center by direct low energy ion beam deposition or by radio frequency self bias glow discharge deposition. The work at Case Western Reserve University was solely concerned with characterizing the films with particular attention paid to developing simple, direct means for categorizing the films of different composition and structure grown by a variety of techniques.

2. DESCRIPTION OF RESEARCH

2.1 Experimental Work

The experimental characterization of the films is described in previously published papers in the open literature and is not repeated here. See Section 3 of this report for a listing of the relevant publications and reports.

2.2 Categorization of "Diamond-like" Hydrocarbon Films

A simple, unambiguous method of categorizing the "diamond-like" hydrocarbon films was desired. The method should involve only simple, unambiguous measurements and should be of sufficient generality to use with solids with very different overall compositions and structures.

The most striking empirical fact about the "diamond like" hydrocarbon films is their anomalously high mass density. For example, a typical film
with atomic fraction of carbon of 0.67 will have a mass density of around 1.8 g/cm$^3$. Films containing up to 50 atomic percent hydrogen will have mass densities greater than 1.5 g/cm$^3$. There are no other hydrocarbon phases with densities this high. For example, polyacetylene, (CH=$\text{=CH}$)$_n$, has a mass density of only 1.16 g/cm$^3$.

The contrast is even more striking when the atomic number density rather than the mass density is used as the basis for comparison. Figure 1 shows the atom number density, $\rho_N$, in gatoms/cm$^3$ versus atom fraction hydrogen, $X_H$, for several classes of hydrocarbons. Several facts are immediately evident from the plot. First, solids with the same basic structure, e.g., the alkanes, fall in clusters on the $\rho_N - X_H$ field. Second, the diamondlike films, indicated by open circles, fall in the region between diamond and adamantane at number densities far greater than conventional hydrocarbons with the same elemental composition.

It is clear from Figure 1 that the "diamond-like" hydrocarbon films may be considered as an entirely new class of hydrocarbon solid. It is further suggested that the term "dense hydrocarbon" is a more appropriate descriptor for these materials than the other common terms, e.g., a-C:H or i-C.

Further details of the categorization of hydrocarbon solids by the methods described above are given in the appendix to this report which is a paper submitted to the journal Thin Solid Films.
Figure 1. Atomic Number Density versus Atom Fraction Hydrogen for Hydrocarbon Solids.
3. PUBLICATIONS

Several publications based on the work during the reporting period were submitted. These include:


4. PERSONNEL

The research was directed by Professor John C. Angus of the Chemical Engineering Department, Case Western Reserve University. All ion deposited films were grown by Mr. Michael J. Mirtich of the NASA Lewis Research Center. All films deposited by radio frequency self bias glow discharge were grown by Mr. Stanley Domitz, also of the NASA Lewis Research Center. Ms. Janet Stultz and Mr. Paul Shiller performed the bulk of the characterization work. Nuclear reaction analyses of the films was provided by Dr. Jack R. MacDonald of the University of Guelph, Guelph, Ontario, Canada.

5. CONCLUSIONS

A simple, unambiguous method for the empirical categorization of solid phases of differing structure and composition based on their atom number density and elemental composition has been developed. The "diamond-like" hydrocarbons are found to belong to a completely new class of hydrocarbon solids. The categorization method may find utility in categorizing other classes of solids, e.g., amorphous hydrogenated silicon.
APPENDIX

Empirical Categorization and Naming of "Diamond-Like" Carbon Films

John C. Angus

To be published in Thin Solid Films
D-EMPIRICAL CATEGORIZATION AND NAMING OF "DIAMONDLIKE" CARBON FILMS

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Submitted to Thin Solid Films
January, 1985

Revised version submitted January, 1986

(14 pages, excluding title page and figure)
Hydrocarbon solids can be empirically categorized by their atomic number density, $\rho_N$, and atomic fraction of hydrogen, $x_H$. Solids with similar molecular structure fall in clusters on the $\rho_N - x_H$ field. "Diamondlike" films formed by ion beam deposition, RF discharge or sputtering have values of $\rho_N$ greater than other carbonaceous solids or hydrocarbon polymers. They fall in the region between diamond and adamantane at values of $\rho_N > 0.2$ g atom/cm$^3$. It is proposed that the terms dense carbon and dense hydrocarbon be used for these solids.
I. INTRODUCTION

"Diamondlike" films formed from electrical discharges in hydrocarbon gases were reported throughout this century\(^1\). Study of the films for their own sake started with the work of Aisenberg and Chabot\(^2\) who produced hard carbonaceous films from carbon ions extracted from a carbon-argon arc. Subsequent confirmation by Spencer\(^3\) led to explosive growth in the field. Representative studies and reviews are given in references 4 through 10.

A large number of plasma discharge and ion beam processes have been employed to produce films with "diamondlike" properties. The high impact energy, over 100 eV, is a common feature of all of these processes. The films can be deposited on many substrates including metals, ceramics, ionic solids and semiconductors. They are more dense, harder and more chemically inert than other solid hydrocarbons or carbonaceous polymers. These properties may be caused by an unusually large number of tetrahedral (sp\(^3\)) carbon-carbon bonds\(^{11-14}\). Details of the film structure must, however, still be considered an open question.

The carbonaceous films can contain significant amounts of hydrogen and in some ways appear analogous to amorphous, hydrogenated silicon (a-Si:H). They differ, however, in that carbon readily forms double and triple bonds. The possible bonding networks for the carbon based films are therefore far more complex than for silicon.
2. ELEMENTAL COMPOSITION AND DENSITY

2.1 Elemental Composition

Numerous studies have confirmed that the "diamondlike" films can contain large amounts of hydrogen, up to 50 atomic percent. There is also evidence, although less compelling, that perhaps one-third to one-half of the hydrogen is not chemically bonded to carbon.

Significant amounts of oxygen, up to 6.7 atomic percent, were reported by Craig and Harding. Angus and Ojha found much less oxygen and some nitrogen in films grown by ion beam deposition and RF discharge in CH/Ar. Oxygen and nitrogen almost certainly arise from residual impurity gases in the deposition chamber.

The inert carrier gas, e.g., Ar, may be incorporated into films during either ion beam or glow discharge processes. Inert gases may be a source of the high densities sometimes observed and also may be the source of anomalous x-ray reflections.

2.2 Density

Overall, macroscopic densities of the "diamondlike" carbonaceous films have been determined by direct measurement of volume and mass or by a sink-float technique using halogenated hydrocarbon liquids. Most of the dense hydrocarbon films (hydrogen atomic fractions ranging from 0.25 to 0.5) have mass densities in the range 1.50 to 2.0 g/cm$^3$.

Significantly higher mass densities, in the range from 2.0 to 3.4 g/cm$^3$, have been reported for films with lower hydrogen content. For example, Miyazawa reported a carbon film with a number density close to that of diamond. Ojha has reported films with densities ranging from 2.0 to 2.67 g/cm$^3$ with H/C atomic ratios near 1/3. The films of Jansen are of interest.
because they have a somewhat lower density than the other dense films. These films were made by sputtering and have relatively less sp³ bonding.

3. EMPIRICAL CATEGORIZATION OF THE FILMS

3.1 Categorisation by Elemental Composition and Density

It is proposed that the films be grouped according to their atom number densities, \( \rho_N \), and atomic composition. The gram atom number density, \( \rho_N \), is just the total number of gram atoms per unit volume.

\[
\rho_N = \frac{\rho_M}{\Sigma x_i A_i}
\]  

where \( \rho_M \) is the mass density, \( x_i \) the atom fraction and \( A_i \) the atomic mass of element \( i \).

In Figure 1 \( \rho_N \) is plotted versus atom fraction hydrogen for a variety of hydrocarbons. The different classes of hydrocarbons fall into distinct groupings on the \( \rho_N - X_H \) field. Also, within a single grouping, the hydrocarbons follow a remarkably consistent pattern. See, for example, the data for the 28 linear alkanes shown in Figure 1. Also note the high number densities of adamantane and diadamantane compared to the other hydrocarbons. Adamantane \((C_{10}H_{16})\) and diadamantane \((C_{14}H_{20})\) are hydrogen saturated microcrystals of diamond.

In Figure 2 some of the data of Figure 1 is re-plotted along with data reported for "diamondlike" carbon films, "plasma polymerized" hydrocarbon films and other solid carbon phases. Note that the "diamondlike" phases, denoted by numbers 1 through 6 in squares, all fall between diamond and adamantane at number densities greater than 0.2 gatom/cm³.
The position of conventional "plasma polymerised" hydrocarbon films (PF) is also of interest. They appear to have a greater number density than conventional hydrocarbon polymers and may be tentatively considered part of the dense hydrocarbon grouping. (Reliable values of both density and composition of plasma polymerised films from a single source were not available. The value of \( \rho_m \) used here was obtained by combining the composition data of Tibbitt \(^{39}\) and the density data of Knickmeyer \(^{40}\).)

The other pure carbon solid phases, which are either based on a graphitic, trigonal structure or completely unsaturated carbon chains, all fall at number densities well below 0.2 gatom/cm\(^3\). The aromatic hydrocarbons (e.g., benzene, naphthalene and anthracene), the linear saturated hydrocarbons (e.g., polyethylene and dodecane) and the oligomers of acetylene (e.g., polyacetylene, hexatriene and butadiene) also fall together in groupings at number densities significantly less than 0.2 gatom/cm\(^3\). Some additional density data for important solid carbonaceous phases are listed in Table 1.
<table>
<thead>
<tr>
<th>Phase</th>
<th>( \rho_\text{atom} ) cm(^{-3})</th>
<th>( \rho_\text{m} ) cm(^{-3})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>0.293</td>
<td>3.515</td>
<td>35</td>
</tr>
<tr>
<td>Dense carbon</td>
<td>-0.23</td>
<td>-2.8</td>
<td>7,30,31</td>
</tr>
<tr>
<td>Dense hydrocarbons</td>
<td>0.21-0.29</td>
<td>1.5-2.0</td>
<td>6,16,24</td>
</tr>
<tr>
<td>Plasma polymers</td>
<td>-0.23</td>
<td>-1.2</td>
<td>39,40</td>
</tr>
<tr>
<td>Adamantane</td>
<td>( \text{C}<em>{10}\text{H}</em>{16} )</td>
<td>0.207</td>
<td>33</td>
</tr>
<tr>
<td>Diadamantane</td>
<td>( \text{C}<em>{14}\text{H}</em>{20} )</td>
<td>0.219</td>
<td>47</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>([\text{CH}_2-\text{CH}_2]_n)</td>
<td>0.199</td>
<td>33</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.188</td>
<td>2.26</td>
<td>35</td>
</tr>
<tr>
<td>Polycumulene</td>
<td>([\text{C}≡\text{C}=\text{C}≡\text{C}]_n)</td>
<td>0.188</td>
<td>38</td>
</tr>
<tr>
<td>Polyacetylene</td>
<td>([\text{CH}=\text{CH}]_n)</td>
<td>0.179</td>
<td>37</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.169</td>
<td>1.25</td>
<td>33</td>
</tr>
<tr>
<td>Polyyne</td>
<td>([\text{C}≡\text{C}≡\text{C}]_n)</td>
<td>0.164</td>
<td>38</td>
</tr>
<tr>
<td>&quot;Amorphous carbon&quot;</td>
<td>mainly trigonal</td>
<td>0.11-0.20</td>
<td>36</td>
</tr>
</tbody>
</table>
3.2 A Caveat

Experimental errors in measuring the mass density and the composition can lead to erroneous placement on the $\rho_n - X_n$ field. Poreosity can lead to erroneously low densities as measured either by sink float or by direct measurement of mass and volume. The presence of significant quantities of unreported heavy atoms, e.g., Ar or W, would give anomalously high values of $\rho_n$. This effect could be significant, but does not appear to alter the basic groupings of Figure 1. Nevertheless, until accurate densities and complete analyses of numerous films become available, the conclusions based on gram atom number density must remain somewhat tentative.

The most likely unreported elements are argon and metals sputtered from the substrate or materials of construction within the deposition chamber. The argon (or other inert gas) is accelerated along with the carbon containing ions and would be embedded in the deposit. If all of the unreported mass present in the samples of Angus et al. is assigned to argon, the atom fraction of argon ranges from 0.013 to 0.034. This is within the range of implanted argon reported for amorphous metals. The effect of unreported argon on the gram atom number densities can be seen from Figure 1. The lower values of the points labelled 4 were obtained assuming all unreported mass to be argon.

4. NOMENCLATURE

No consistent nomenclature has been developed for describing these unusual hydrocarbon and carbon films. A variety of names have been used, e.g., diamondlike films, hard carbonaceous films, hard carbon, a-C:H and i-carbon. Different names have been used to describe very similar materials and, conversely, the same name used to describe very different materials.
Figure 1 provides a simple basis for the naming of the films. Films with 
\( \rho_n > 0.2 \text{ g atoms/cm}^3 \) are designated "dense carbonaceous films." Films containing significant amounts of hydrogen are called "dense hydrocarbon films." The pure carbon films will be called "dense carbon" if \( \rho_n > 0.2 \text{ g atoms/cm}^3 \). The advantage of the descriptor "dense" is that it is based solely on measurable macroscopic quantities. It implies nothing about the structure of the films nor the mechanism of formation as do some of the other names.

The term "diamondlike" has been widely used by many authors because of similarities in properties between the films and diamond. If it is applied, it clearly should be restricted to films known to be dominated by \( sp^3 \) tetrahedral bonding. The abbreviation a-C:H, which is taken by analogy to amorphous, hydrogenated silicon, would appear to be only appropriate in those cases where it is known that the film is amorphous.

The term i-carbon or i-C has been suggested by Weissmantel. The i refers to the fact that the films are usually made by deposition of accelerated ions. This nomenclature also appears somewhat less appropriate. For example, many of the films of interest contain large amounts of hydrogen as well as carbon. Secondly, the ions do not appear to be intrinsic to the growth process. For example, in sputter deposition the impacting species are largely neutral. Also, some other recently reported processes do not involve significant numbers of ionized species.

The term "hard carbonaceous" films has also been suggested and used widely. This designation, while appropriate in many cases, could also apply to the hard, trigonally bonded films produced by evaporation. Furthermore, hardness is difficult to quantify, especially for thin films.
3. DISCUSSION

The proposed method of categorization of hydrocarbon solids by atomic composition and number density must be regarded as essentially empirical and contains no detailed information about film structure. Nevertheless, the fact that solids with similar structures fall in well-defined clusters in the $a_H - X_H$ field can provide a simple means of comparing complex solid phases derived from different sources. For example, the fact that the "diamond-like" films appear to fall between diamond and adamantane at number densities significantly higher than those of all trigonal or linear structures is of significance. The position of the dense carbonaceous films may indeed reflect a local structure based primarily on $sp^3$ tetrahedral bonding. (On the other hand, one can argue that such unusually high number densities are evidence of errors in the measured mass densities or elemental analyses.)

Also, the evaporated carbons, formed by resistance, electron beam or laser evaporation of graphite fall at number densities significantly lower than films formed by the more energetic processes, such as sputtering, RF discharge or ion beam deposition. This result is consistent with the current view that the evaporated films are dominated by $sp^2$ trigonal bonding, whereas the films formed at higher impact energies have a very significant amount of $sp^3$ tetrahedral bonding. However, other structures could also be responsible for the high number densities. For example, microscopic internal surfaces covered with chemisorbed atomic hydrogen may be one. Trapped molecular hydrogen would not appear to give rise to high number densities since the atomic number density of solid $H_2$ is only 0.0694 gatom/cm$^3$.

It must be emphasized again, however, that much more composition and density data of greater accuracy must be obtained before definitive statements about the dense carbonaceous films can be made. It would also be of con-
siderable interest to test proposed local structural models of the dense carbonaceous films by computing the value of $\rho_w$.

One final point deserves mention. Single crystal diamond has an anomalously high atomic density. In fact, it appears to have the highest number density of any common solid at atmospheric pressure.

6. ACKNOWLEDGEMENTS

The financial support of the NASA Lewis Research Center, Cleveland, Ohio (USA) is gratefully acknowledged. Ms. Judy Yan assisted in data collection for Figure 1 and Table 1.
REFERENCES


Figure 1: Gram atom number density $^a$ versus atom fraction hydrogen for a series of hydrocarbons

- adamantane$^{35}$ and diadamantane$^{47}
- $n$-alkanes $C_3$ through $C_{29}$ and $C_{32}$$^{48,49}
- Polyacetylene, 1,3,5 hexatriene and 1,3 butadiene$^{48,49}
- chrysene, anthracene, naphthalene, pyrene, phenanthrene and benzene$^{48,49}$

$^a$ Density data is taken at 25°C and 1 atm. For the $n$-alkanes $C_7$ and higher, subcooled liquid densities were used to eliminate the density difference due to phase change.
The diagram illustrates the relationship between the atomic number density (g/mole/cc) and the atom fraction of H. The graph shows data points for different categories:

- Adamantanes
- Oligomers of Acetylene
- Condensed Ring Aromatics
- n-Alkanes

The x-axis represents the atom fraction of H, ranging from 0.35 to 0.75, while the y-axis represents the atomic number density, ranging from 0.10 to 0.24.
Figure 2: Gram atom number density versus atom fraction hydrogen

"Diamondlike" Solids:
1. Ojha
2. Mysics
3. Miyasawa
4. Angus
5. Jansen
6. Bubenser

Other Phases:
AD. adamantane
AM. amorphous carbon
AN. anthracene
BD. butadiene
BZ. benzene
D. diamond
DO. dodecane
GL. glassy carbon
GR. graphite
HT. hexatriene
NA. naphthalene
PA. polycetylene
PE. polyethylene
PL. polyyne
PP. plasma polymers
SI. silicon