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16. Abstract

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.

17. Key Words (Suggested by Author(s)) Diamond-like hydrocarbons Dense hydrocarbon films Atom number density	18. Distribution Statement Unclassified, Unlimited

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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, $(CH=CH)_n$, 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 comparision. Figure 1 shows the atom number density, ρ_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 ρ_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.
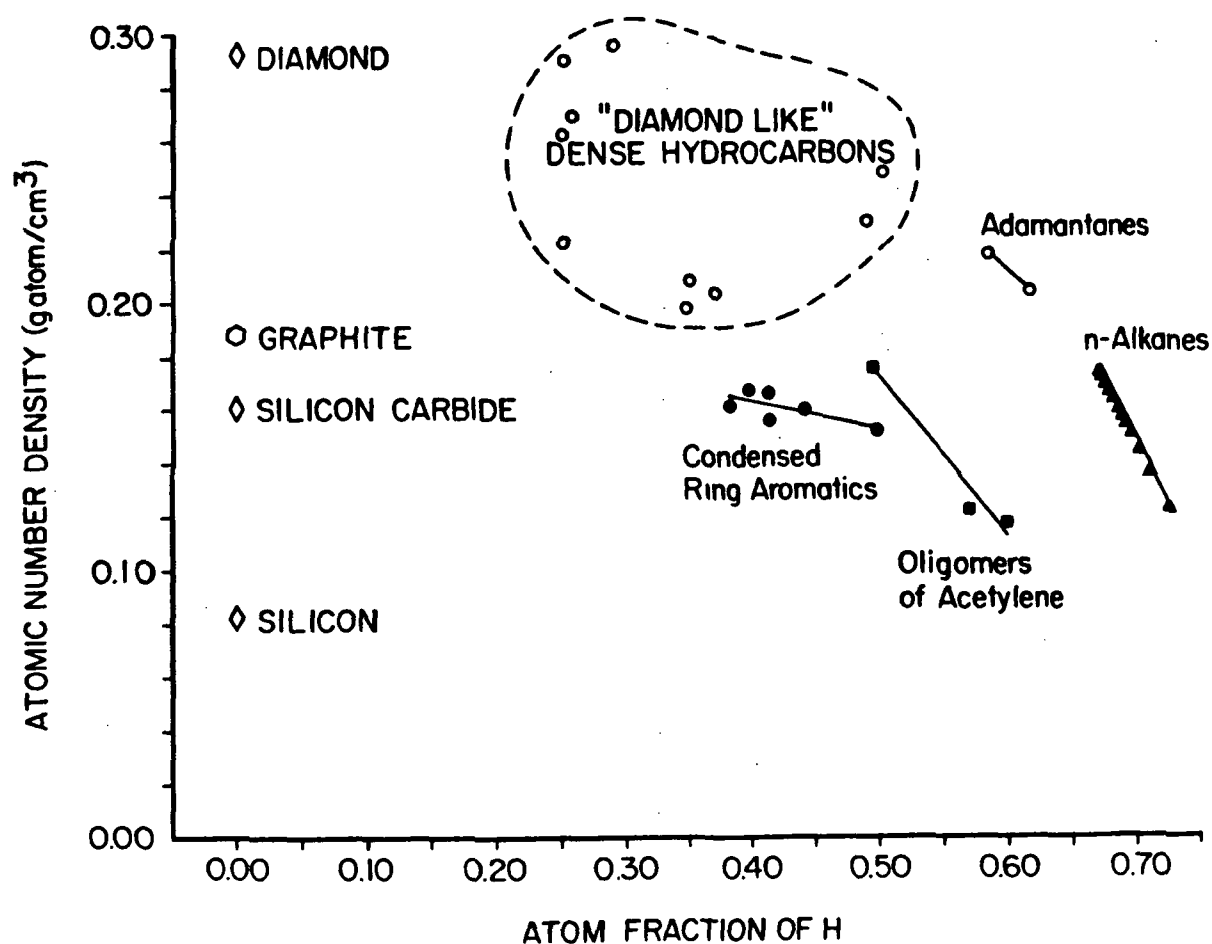
3. PUBLICATIONS

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

1. J.C. Angus, J.E. Stultz, P.J. Shiller, J.R. MacDonald, M.J. Mirtich and S. Domitz, "Composition and Properties of the So-called 'Diamond-like' Amorphous Carbon Films," Thin Solid Films 118(3), 311-20 (1984)

2. J.C. Angus, P. Koidl and S. Domitz, "Dense Carbonaceous Films with 'Diamond-like' Properties" in "Plasma Deposition of Thin Films," J. Mort and F. Jansen, Editors, CRC Press, Boca Raton, FL, in press.

3. J.C. Angus, "Empirical Categorization and Naming of 'Diamondlike' Carbon Films," accepted for publication in Thin Solid Films.

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

D-EMPIRICAL CATEGORIZATION AND NAMING OF "DIAMONDLIKE" CARBON FILMS

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(14 pages, excluding title page and figure)

SUMMARY

Hydrocarbon solids can be empirically categorized by their atomic number density, ρ_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 ρ_N greater than other carbonaceous solids or hydrocarbon polymers. They fall in the region between diamond and adamantane at values of $\rho_N > 0.2$ gatom/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.

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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[15-25]. There is also evidence, although less compelling, that perhaps one-third to one-half of the hydrogen is not chemically bonded to carbon[24,25,26].

Significant amounts of oxygen, up to 6.7 atomic percent, were reported by Craig and Harding[17]. Angus[24] and Ojha[16] found much less oxygen and some nitrogen in films grown by ion beam deposition and RF discharge in CH_4/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[27]. Inert gases may be a source of the high densities sometimes observed and also may be the source of anomalous x-ray reflections[28,29].

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[7,8,30,31]. For example, Miyazawa[32] reported a carbon film with a number density close to that of diamond. Ojha[16] 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[14] are of interest

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because they have a somewhat lower density than the other dense films. These films were made by sputtering and have relatively less sp^3 bonding.

3. EMPIRICAL CATEGORIZATION OF THE FILMS

3.1 Categorization by Elemental Composition and Density

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

$$\rho_N = \frac{\rho_M}{\Sigma x_i A_i} \tag{1}$$

where ρ_M is the mass density, x_i the atom fraction and A_i the atomic mass of element i.

In Figure 1 ρ_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/cm^3.

The position of conventional "plasma polymerised" hydrocarbon films (PP) 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 ρ_N 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 1

Densities of Carbon and Hydrocarbon Phases

Phase		$\rho_N \frac{gatom}{cm^3}$	$\rho_M \frac{g}{cm^3}$	Reference
Diamond		0.293	3.515	35
Dense carbon		~0.23	~2.8	7,30,31
Dense hydrocarbons		0.21–0.29	1.5–2.0	6,16,24
Plasma polymers		~0.23	~1.2	39,40
Adamantane	$C_{10}H_{16}$	0.207	1.07	33
Diadamantane	$C_{14}H_{20}$	0.219	1.21	47
Polyethylene	$[CH_2-CH_2]_n$	0.199	0.93	33
Graphite		0.188	2.26	35
Polycumulene	$[C=C=C=C]_n$	0.188	2.25	38
Polyacetylene	$[CH=CH]_n$	0.179	1.16	37
Anthracene		0.169	1.25	33
Polyyne	$[C\equiv C-C\equiv C]_n$	0.164	1.97	38
"Amorphous carbon"	mainly trigonal	0.11–0.20	1.35–2.4	36

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3.2 A Caveat

Experimental errors in measuring the mass density and the composition can lead to erroneous placement on the ρ_N - X_H field. Porosity 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 ρ_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[27,28,29]. If all of the unreported mass present in the samples of Angus et al.[24] 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[27]. 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.

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Figure 1 provides a simple basis for the naming of the films. Films with $\rho_N > 0.2$ gatom/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 $\rho_N > 0.2$ gatom/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[5]. 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[41]. Also, some other recently reported processes do not involve significant numbers of ionized species[42,43,44].

The term "hard carbonaceous" films has also been suggested[4] and used widely. This designation, while appropriate in many cases, could also apply to the hard, trigonally bonded films produced by evaporation[45]. 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 ρ_H - X_H field can provide a simple means of comparing complex solid phases derived from different sources. For example, the fact that the "diamondlike" 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[45], whereas the films formed at higher impact energies have a very significant amount of sp^3, tetrahedral bonding[11-14]. 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.[46]

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 car-
bonaceous films by computing the value of ρ_N.

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

6. ACKNOWLEDGEMENTS

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Figure 1: Gram atom number density[a] versus atom fraction hydrogen for a series of hydrocarbons

X   adamantane[33] 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_{17} and higher, subcooled liquid densities were used to eliminate the density difference due to phase change.
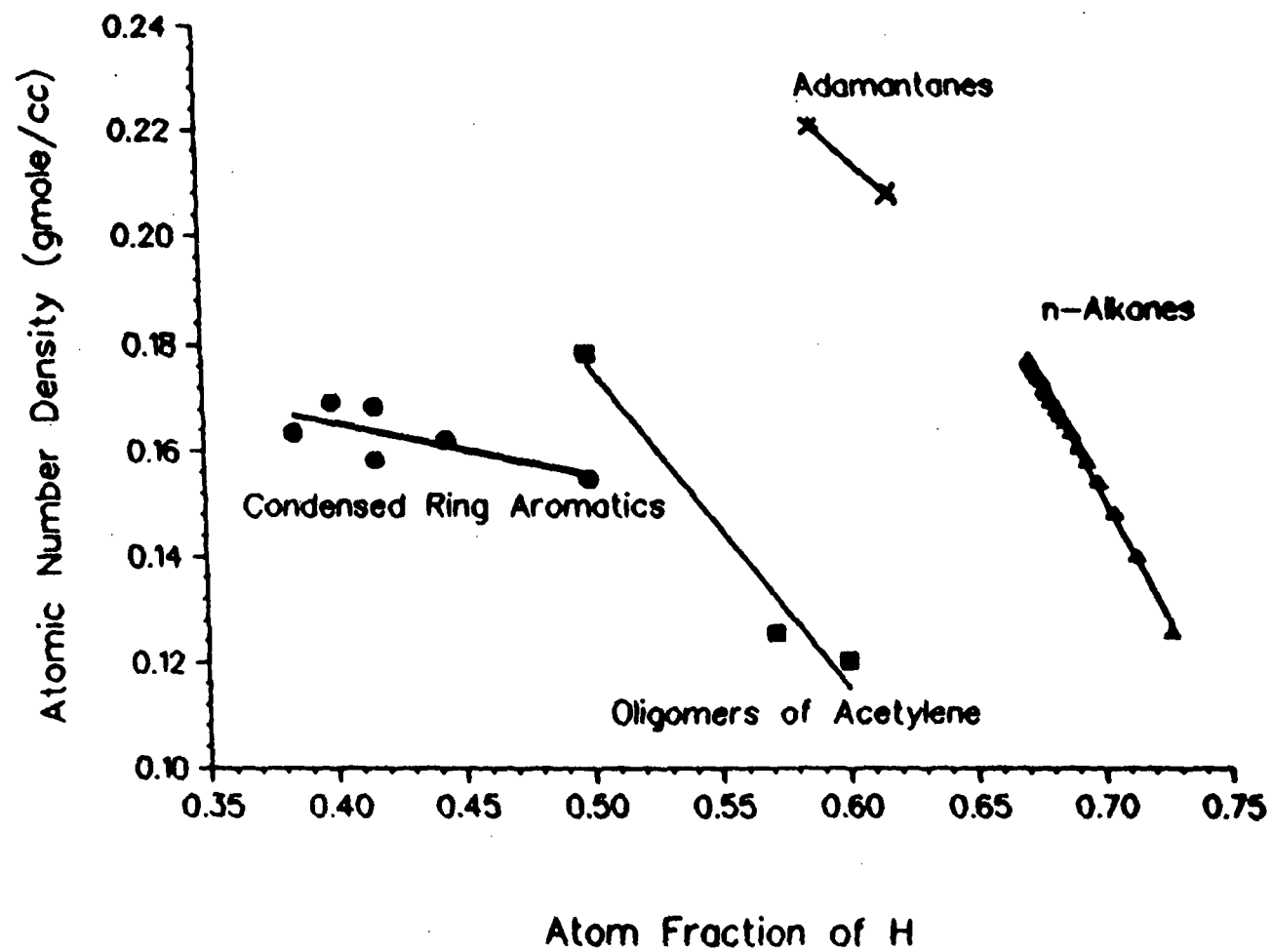
Figure 2: Gram atom number density versus atom fraction hydrogen

"Diamondlike" Solids:

1 Ojha[16]

2 Nyaiesh[20]

3 Miyazawa[32]

4 Angus[10]

5 Jansen[14]

6 Bubenzer[6]

Other Phases:

AD adamantane[33]

AM amorphous carbon[34]

AN anthracene[33]

BD butadiene[33]

BZ benzene[33]

D diamond[35]

DO dodecane[33]

GL glassy carbon[36]

GR graphite[35]

HT hexatriene[33]

NA naphthalene[33]

PA polyacetylene[37]

PE polyethylene[33]

PL polyyne[38]

PP plasma polymers[39,40]

SI silicon[33]

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ORIGINAL PAGE IS
OF POOR QUALITY