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Dual Ion Beam Deposition of Carbon Films With Diamondlike Properties

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DUAL ION BEAM DEPOSITION OF CARBON FILMS WITH DIAMONDLIKE PROPERTIES

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SUMMARY

A single and dual ion beam system was used to generate amorphous carbon films with diamondlike properties. A methane/argon mixture at a molar ratio of 0.28 was ionized in the low pressure discharge chamber of a 30-cm-diameter ion source. A second ion source, 8 cm in diameter was used to direct a beam of 600 eV Argon ions on the substrates (fused silica or silicon) while the deposition from the 30-cm ion source was taking place. Nuclear reaction and combustion analysis indicate H/C ratios for the films to be 1.00. This high value of H/C, it is felt, allowed the films to have good transmittance. The films were impervious to reagents which dissolve graphitic and polymeric carbon structures. Although the measured density of the films was approximately 1.8 gm/cm^3, a value lower than diamond, the films exhibited other properties that were relatively close to diamond. These films were compared with diamondlike films generated by sputtering a graphite target.

INTRODUCTION

There have been many publications recently reporting efforts to produce thin carbon films with diamondlike properties. A variety of plasma and ion beam techniques have been employed to generate the carbon films. The films can be deposited by rf plasma decomposition of a hydrocarbon gas[1,2] or other alkanes,[3] by low energy carbon ion beam deposition[4,5] or by ion plating and dual beam techniques.[6] Weissmantel, et al.[6] refer to these films as i-carbon (i-c) implying that some type of ion bombardment or ion beam is involved in the film preparation.

Because the films have been generated using a wide variety of techniques, the physico-chemical properties of such films vary considerably. In general these films have characteristics that are desirable in a number of applications. They have potential in power electronics as insulated gates for field effect transistors or as doped semi-conductors. They also may find use as protective coatings for FET and optical components, integral coatings for solar cells or laser windows in the infrared. Successful realization of these applications is contingent on effective production of these films and their characteristics. These characteristics can be changed by varying the deposition technique and potentially tailored to meet the needs of the particular application. With this in mind films were produced at NASA Lewis Research Center by using methane (CH_4) and argon in either single or dual ion beam sources. This paper presents the process techniques and the characteristics of these films and compares them with diamondlike films generated by Banks and Rutledge[5] using an ion source to sputter deposit carbon from a graphite target.

ION SOURCE AND DEPOSITION PROCEDURE

A 30-cm-diameter ion source with its optics masked to 10 cm in diameter was used to directly deposit i-carbon films (fig. 1). The ion source, developed for electric propulsion technology, uses argon gas in the hollow cathode located in the main discharge chamber, as well as in the neutralizer.[7] After a discharge is established between the cathode and anode, methane (CH_4) is introduced through a manifold into the discharge chamber. For the depositions presented in this paper the molar ratio CH_4 to argon was 0.28. This ratio was found to be ideal for generating films. If the CH_4/Ar ratio was too large the discharge extinguished. No films were observed at low a CH_4/Ar ratios since this condition did not allow a net deposition of C atoms due to the more dominant sputtering effects of the Ar ions. The ideal energy level for deposition of i-carbon films has been reported to be between 100 and 150 eV.[3,4] In these experiments the total ion beam energy is the sum of the discharge voltage and the screen grid voltage. Therefore, for a discharge voltage of about 50 volts the screen grid voltage was approximately 50 volts. At this low value of screen grid voltage it was necessary to increase the accelerator voltage more negative than usual (to around -500 volts) to extract a beam. Typically current densities at these conditions were 1 ma/cm^2 at a distance 2.5 cm axially downstream of the grids.[8]

Knowing the current density and the knowledge that divergent field ion sources can be operated at low ion extraction voltages (normal conditions usually utilize screen grid voltages of 1000 volts) it was possible to design an experiment using a single ion source (30 cm) with CH_4/Ar at 100 eV and current densities of 0.2 ma/cm^2. This current density was suggested by S. Aisenberg[4] as an upper limit current density. Films were deposited at these

conditions on Si and SiO_2 at deposition rates as high as 71Å/min to film thicknesses as great as 1.5 um.

It is believed that the amorphous carbon films are produced under conditions where both growth and sputtering occur simultaneously increased sputtering may decrease the number of graphite precursors incorporated in the films and hence improve film quality.

In addition Marinow and Dobrew[9] have found that active sites for nucleation are created and the growth and coalesence of the nuclei enhanced due to an increased mobility of the condensing atoms when film structures are bombarded by inert gas beams. With these factors in mind, a dual beam system was created by adding an 8-cm diameter argon ion source. This system, shown in Fig. 1, was used to generate another set of i-carbon films. The 8-cm source, using a filament cathode, was located at a 12° angle with respect to the 30-cm source and 25 cm from the substrate. There was no observed interaction between the two sources or the ion beams during operation.

The 8-cm ion source was used to direct a beam of energetic (200 to 600 eV) argon ions at a current density of 25 $\mu a/cm^2$ on the substrates while the deposition from the 30-cm ion source was taking place. When the ion energy of this second beam was greater than 550 eV, no net film formation was found. The beams were approximately mono-energetic; however no mass selection was attempted.

RESULTS AND DISCUSSION

Arrival rates at surfaces. The species arriving at the surface can be divided into two categories: 1) Primary ions including Ar^+, C^+ and hydrocarbon fragments of the general form $C_mH_N^{+Z}$, and 2) a flux of unchanged species arising from residual background gas. Ideally, one would like the ion beam flux, J_I, to be much greater than the flux from residual

gases, J_R. Typical conditions in the vacuum chamber were: residual background pressure, $5x10^{-7}$ Torr; operating pressure, $2x10^{-5}$ Torr (away from target) and $2x10^{-4}$ Torr (near target). At a pressure of 10^{-7} torr, a temperature of 300° K and an average molecular weight of 25 a simple kenetic theory of gases calculation shows that $J_I/J_R \cong 10$.

In the above estimate the residual background pressure was used since it is a measure of the atmospheric gas contamination level (the increase in pressure during operation arises from unionized methane and argon). Setting $P=2x10^{-4}$ torr one finds J_I/J_R is $\sim 2x10^{-2}$. Thus, the vast majority of species hitting the surface are actually unionized source gas molecules rather than ions.

COMPOSITIONAL CHARACTERISTICS

Auger spectra of the i-carbon films showed no evidence of any elements other than carbon and small amounts of argon and oxygen. The films were remeasured after argon ion sputter profiling with an ion energy of 2000 volts and a current density of 25 $\mu a/cm^2$. The oxygen signal disappeared, but the argon signal was enhanced. High resolution Auger Spectra obtained from a single crystal of pyrolytic graphite, an ion beam deposited carbon film sample and natural diamond are shown in Fig. 2. The lineshape for the ion beam deposited carbon film lies somewhere between those of pyrolytic graphite and diamond. The shoulder in the graphite spectrum at 250 eV is present in the i-carbon film spectrum, but not as pronounced. This result was consistently observed on numerous samples. The spectrum for natural diamond shows no shoulder and the main peak is shifted to higher energies. This latter effect may be caused by some charging of the sample.

After sputtering, the spectra from the ion deposited carbon film and the natural diamond became identical to that obtained from the pyrolytic

graphite. This result is in agreement with earlier work which showed ion beam sputtering causes the surface of diamond to give a "graphitic" Auger signal.[10,11] One should also note that the escape depth of the 270 eV Auger electrons is only 7Å[12]. Consequently, in all cases only the outermost surface layers were sampled. These would be the most prone to graphitization. It is, therefore, significant that differences between the ion beam deposited films and graphite were observable.

An example of a Secondary Ion Mass Spectroscopy (SIMS) spectrum from a dual beam deposited film on a silicon substrate is shown in Fig. 3. There are a cluster of peaks at 12, 13, 14 and 15 AMU from the hydrocarbon fragments C^+, CH^+, CH_2^+, and CH_3^+. The peak at 14 AMU could also be assigned to N^+; even though the lower sensitivity AUGER analysis indicated no nitrogen present in the films. There is a strong H^+ peak at 1 AMU and a cluster of hydrocarbon peaks at 26, 27, 28 and 29 AMU. It has been noted by Benninghoven[13] that when multiatom ionic clusters are emitted from the surface, e.g., CH_2^+, these atoms were bound together in the original solid. Therefore, it appears likely that the ion deposited film contains chemically combined hydrogen. It has been shown that for these films,[14] using semiquantitative infrared spectroscopy, the ratio of chemically bonded hydrogen to carbon is between 0.03 and 0.44. However, nuclear reaction and combustion analysis,[15] which are in good agreement, indicate that the H/C atom ratio is close to unity. This difference between the two measurement techniques probably arises from the presence of nonbonded hydrogen in the films.

The electron diffraction pattern of the films generated using either the single ion source or dual beam method was found to be characteristic of an amorphous solid. Angus, suggested that these films consist of a structure

that is a random network of methylene and double bonded carbon linkages and tetrahedrally coordinated carbon atoms.[14]

OPTICAL PROPERTIES OF FILMS

The spectral transmittance, reflectance and absorptance of the films deposited on fused silica were obtained using the Gier-Dinkle® integrating sphere and the techniques described in Ref. 16.

Shown in Fig. 4 is the spectral transmittance for i-carbon films varying in thickness from 800 Å to 3300 Å. These films were obtained using the dual beam ion source. Figures 5 and 6 show the corresponding spectral reflectance and absorptance for these same films. At short wavelengths the film all show a large decrease in transmittance with a corresponding large increase in absorptance. For film thicknesses between 800 and 1500 Å there are only small differences in transmittance at all wavelengths. Increasing the i-carbon film thickess to 3300 Å has only a small effect on the transmittance for wavelengths greater than 8000 Å, but reduces the transmittance to as low as 10 percent at 4000 Å. Most of this transmittance loss for the 3300 Å thick film is due to the corresponding increase in absorptance (fig. 6). The thinner films (800 to 1500 Å) look clear to yellowlike in appearance and the thicker 3300 Å film brown.

The spectral transmittance, reflectance and absorptance for the films generated using the single ion source are similiar to those generated using the dual beam source, but have a lower spectral transmittance for films greater than 1200 Å thick. This is evident in Fig. 7 where the spectral transmittance is shown for two i-carbon films of similar thickness (1500 Å) generated using CH_4 in the dual beam and single ion source. Also shown in Fig. 7 are spectral data for an i-carbon film 1700 Å thick, obtained by ion beam sputtering of a carbon target.[5] The transmittance was measured only between 4000 and

8000 Å for this film and is very low when compared to the CH_4 deposited films. The low transmittance of the film of Ref. 5 may be due to its low hydrogen content, in comparison to the CH_4-derived i-carbon films. The 1500 Å thick dual beam film has greater transmittance at all wavelengths when compared to the 1500 Å thick single beam film. The increased absorption most likely arises from the presence of systems of conjugated double bonds within the film although the presence of oxygen could also play a role. Both the graphitic precursors and oxygen would be expected to be reduced by the increased sputtering from the second beam.

Also shown in Fig. 7 is the spectral transmittance for a 500 Å film generated using CH_4 in the single 30-cm ion source. This film has transmittance values greater than 90 percent at wavelengths greater than 7000 Å. Since the transmittance is increasing with wavelength, these films could have use in high energy laser applications as a chemically inert encapsulant for coated optics. If the transmittance of the films with high hydrogen content could be improved further, they could find use as integral cover slides for solar cells. This might be accomplished by adding hydrogen to the films during the deposition process or by increasing the energy level of the second ion source to obtain better sputter removal of oxygen and conjugated, graphitic structures.

Listed in table I are values of H/C ratio, optical band gap, index of refraction, absorption coefficient and solar transmittance for CH_4-derived films generated using the single or dual beam ion sources, and, sputter deposited films of Ref. 5. Certain properties are enhanced by using a dual beam system, mainly the solar transmittance which is higher, as is the index of refraction, and a lower absorption coefficient, when compared to the single ion source films. The optical band gap and density for the single and dual

beam system films are similar. The films obtained by Banks and Rutledge[5] have a higher band gap, but a lower solar transmittance (by a factor of two), when compared to the CH_4 single or dual beam films. These differences between the films of Ref. 5 and single or dual beam films are probably due to the difference in hydrogen content of the films.

CHEMICAL AND PHYSICAL PROPERTIES

The i-carbon single and dual beam films were subjected to a solution of 3 parts H_2SO_4 and 1 part HNO_3 (concentrated acids, by volume) at 80° C for periods up to 20 hours. The films on silicon were unaffected by the reagent. The films on fused silica showed varied behavior. In some cases they were unaffected by the reagent and in others the film was removed from the substrate, but not fully dissolved. These results clearly indicate that the best films, especially those on silicon, are far more resistant to chemical etching than normal polymeric hydrocarbons or graphite. This suggests appreciable tetrahedral bonding and the potential use of the i-carbon films as chemical and/or a diffusion barrier for microelectronic or optical components.

Transmission electron microscopy at 30 000 X showed the films to be smooth and essentially free of features. No pinholes or other defects were observed.

Also listed in table I are values of resistivity, density, and adherence for films generated using CH_4 with the single or dual beam ion sources, and sputter deposited films of Ref. 5. The films obtained by Banks and Rutledge[5] have a resistivity similar to the dual or single beam films, but have a higher density.

The adherence of the films on quartz was measured following the procedure used by Mirtich.[17] The adherence of the films generated with either the

single or dual beam systems were as good as the maximum adherence of the Sebastian Adherence Tester® used in the measurement (~5.5×10^7 N/m^2 or 8000 psi). The film adherence was so good that for some films, portions of quartz gave way with the film still intact.

Some CH_4 films deposited with the dual beam on Si have been kept for four years and show no visible signs of deterioration. However, the thickest film, 1.75 μm, deposited using the single ion source, spalled from the substrate within several weeks.

The films are clearly not graphitic, i.e., they are quite transparent in the visible, are nonconducting and are impervious to reagents which dissolve graphitic and polymeric carbon structures. The films appear to have some characteristics similar to diamond (transparent, chemically inert, high resistance) but do not have the long range order of the diamond crystal structure. Hence these films, with this collection of properties, may be loosely called "diamondlike."

These films are currently under evaluation for use as insulating gates for field effect transistors or as doped semiconductors by Vic Kapoor, at the University of Cincinnati, Dept. of Electrical and Computer Engineering under NASA Grant NCC 3-36.

CONCLUDING REMARKS

Single or dual ion beam systems using CH_4/Ar gases were used to deposit amorphous carbon films on quartz and silicon. Auger spectra of the films show no evidence of any elements other than carbon and small amounts of argon and oxygen. SIMS spectra show strong H^+ peaks at 26, 27, 28 and 29 AMU. Nuclear activation and combustion analysis indicate that the hydrogen to carbon ratio of the films is close to unity. The large amount of hydrogen in these methane derived films, generated with either the single or dual beam results in high

transmittance values when compared to films generated by sputter deposition from graphite targets. The films generated with the dual beam system had higher values of spectral transmittance than those made with the single ion source.

Transmission electron microscopy at 30 000 times magnification showed the films to be smooth and essentially free of features. The films were impervious to reagents which dissolve graphitic and polymeric structures. The optical band gap and density of the films generated with either the single or dual beam were similar and lower than those produced with a graphite target. The adherence of the films on quartz was greater than 8000 psi. The films appear to have some characteristics similar to diamond, but do not have the long range order of the diamond crystal structure.

Modification in the hydrogen content of the films and evaluation for specific application are currently under way.

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TABLE I. - OPTICAL, CHEMICAL AND PHYSICAL PROPERTIES OF I-CARBON FILMS GENERATED USING CH_4 WITH SINGLE OR DUAL BEAM ION SOURCES, AND SPUTTER-DEPOSITION OF GRAPHITE

	30 cm CH4/A~ = 28 percent	Dual beam CH4/A~ = 28 percent	Graphite target
H/C ratio	----------	1.0	Low
Resistivity, Ω-cm	8.66×10^6	3.35×10^6	5.29×10^6
Optical band gap (eV)	0.382	0.343	0.909
Density, gm/cm^3	1.8	1.8	2.2
Index of refraction	2.0	2.46	--------
Absorption coefficient/cm at 5000 Å	5.15×10^4	4.26×10^4	7.26×10^4
Solar transmittance $t = \frac{\int Q(\lambda)T(\lambda)d(\lambda)}{\int Q(\lambda)d\lambda}$	0.519	0.648	0.134
	Film = (1500 Å thick)	(1500 Å)	(1700 Å)
Adherence (Quartz)	$>5.5 \times 10^7$ N/m^2 >8000 psi	$>5.5 \times 10^7$ N/m^2 >8000 psi	

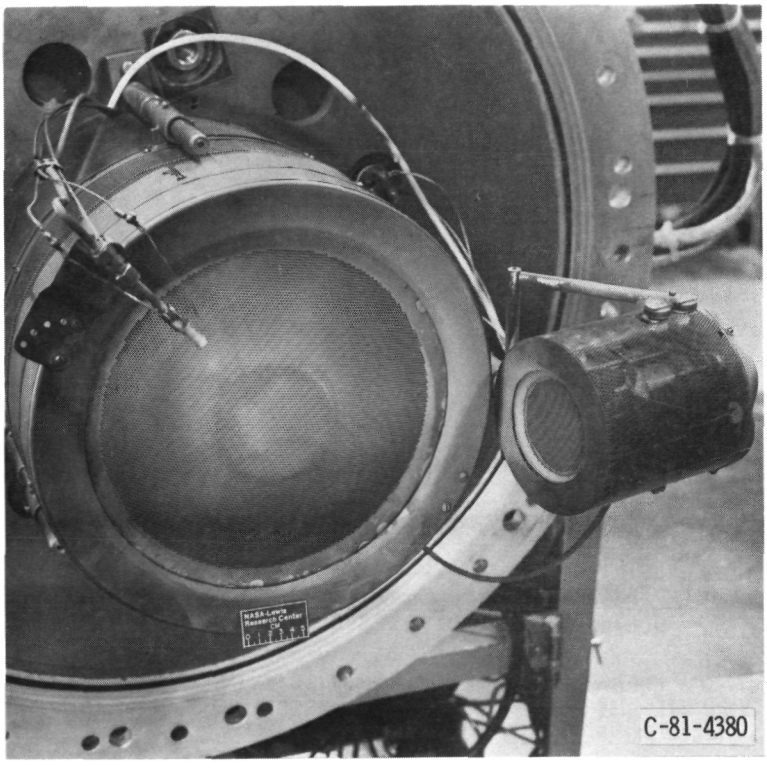

Figure 1. - Dual beam ion source for deposition of films with diamond-like properties.

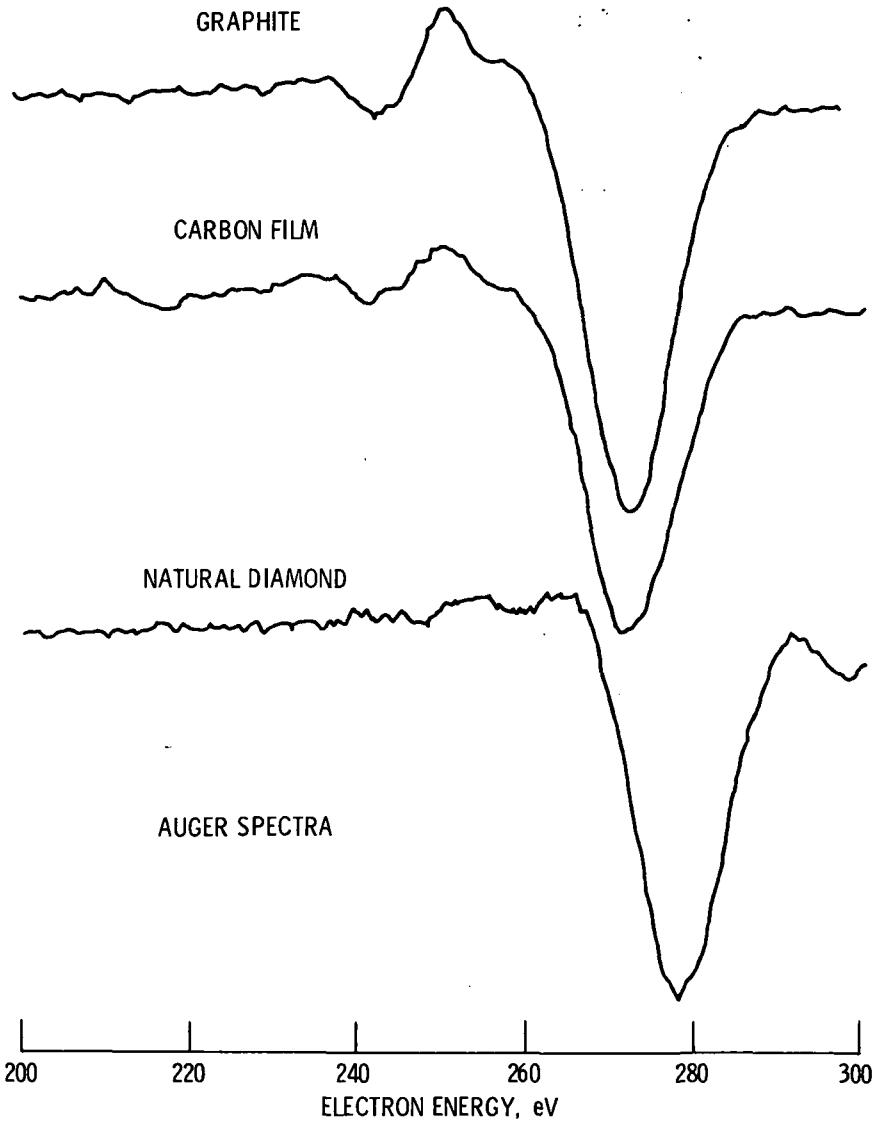

Figure 2. - Auger spectra of pyrolytic graphite, ion deposited carbon film and natural diamond.

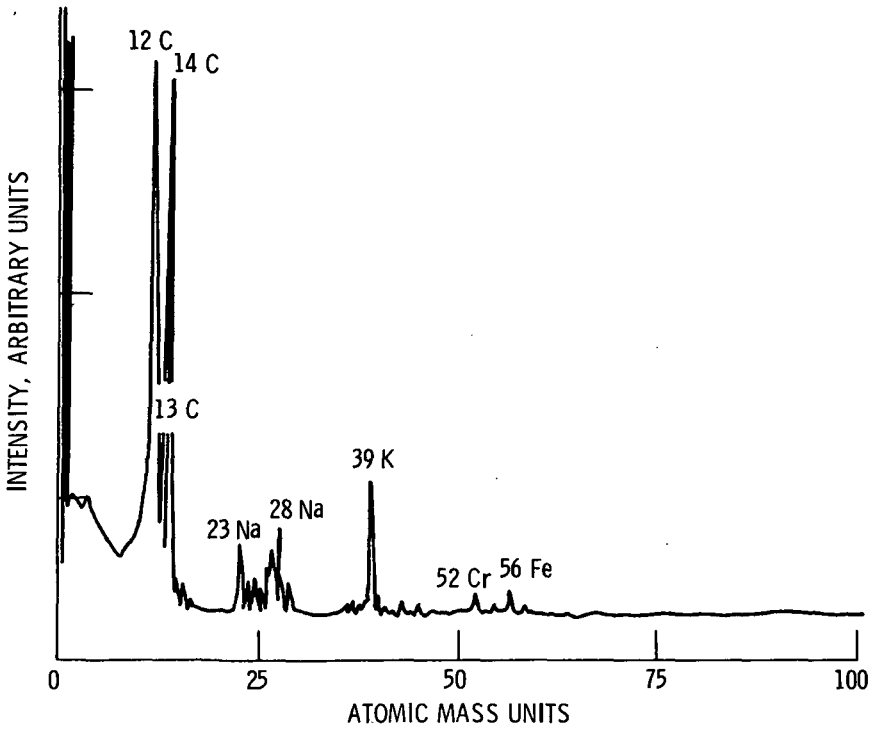

Figure 3. - Secondary ion mass spectrum of ion-deposited carbon film on silicon after 17 minutes of argon ion sputtering.

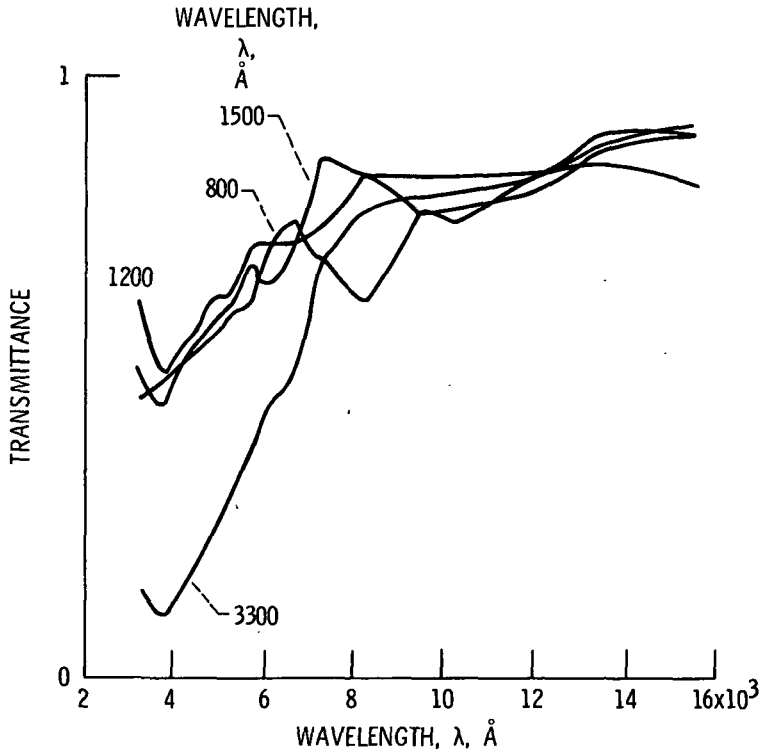

Figure 4. - Transmittance versus wavelength for various thickness i-carbon films generated using CH_4 in the dual beam system.

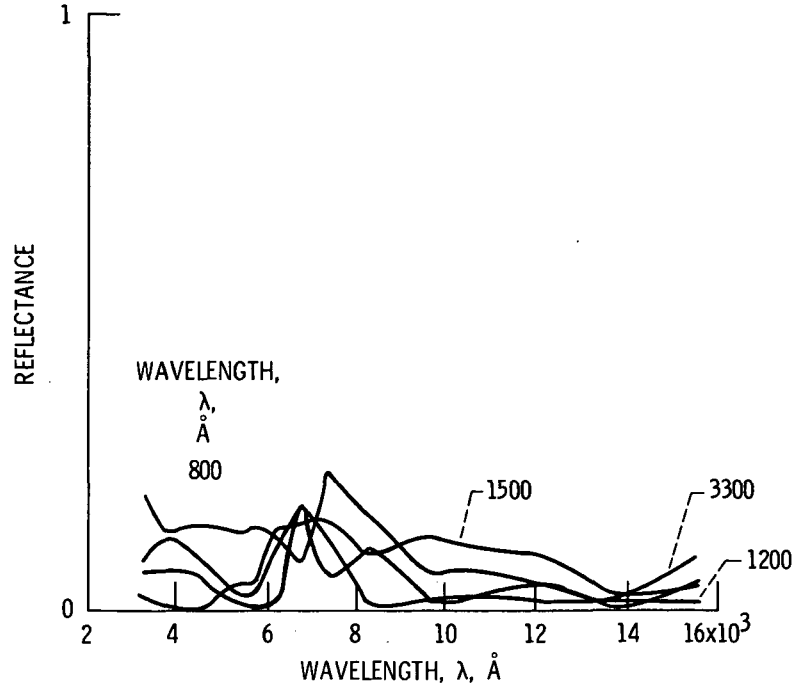

Figure 5. - Reflectance versus wavelength for i-carbon films generated using CH_4 in the dual ion beam system.

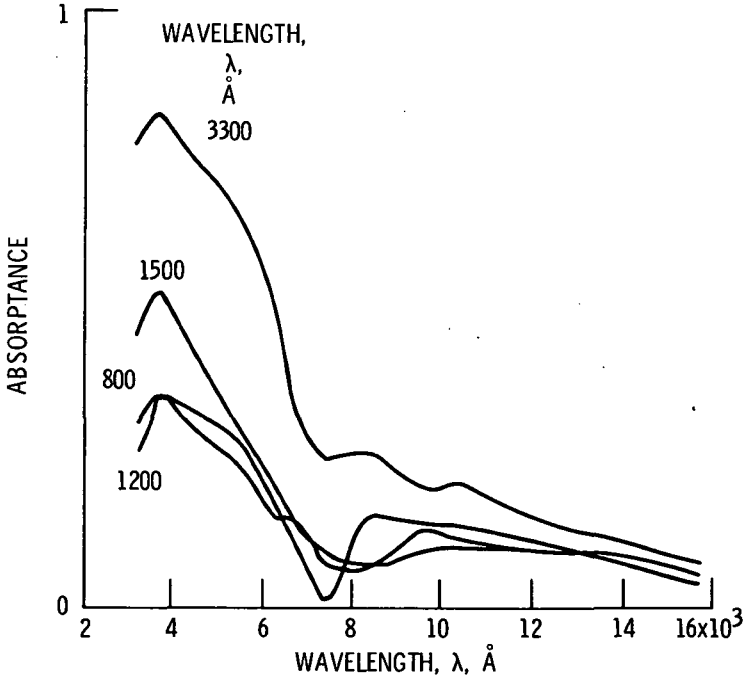

Figure 6. - Absorptance versus wavelength for i-carbon films generated using CH_4 in the dual beam ion sources.

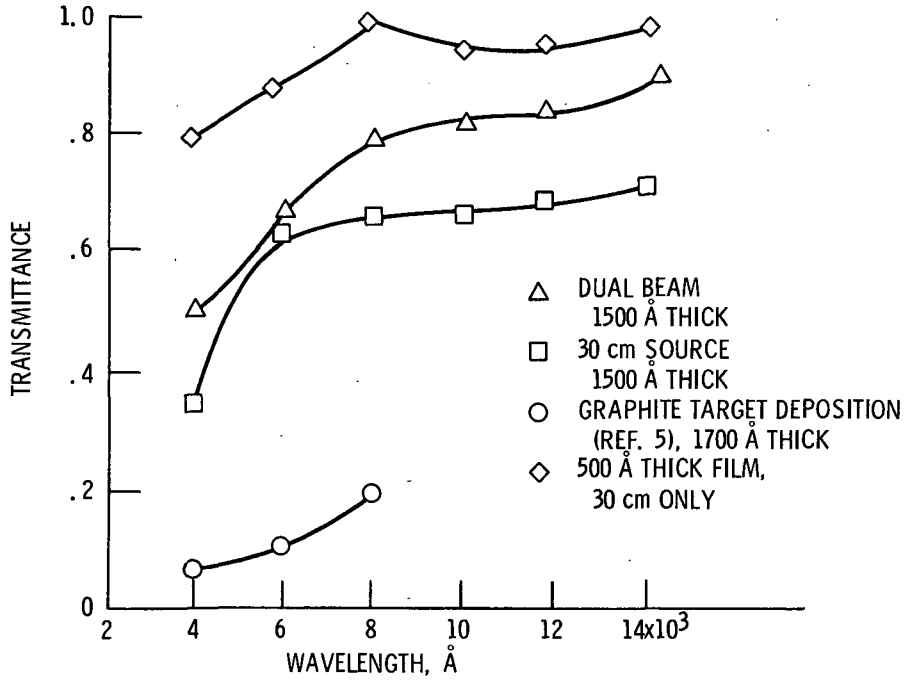

Figure 7. - Transmittance versus wavelength for i-carbon films using CH_4 in dual beam or single ion sources and graphite target deposition of ref. 5.

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15. Supplementary Notes

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16. Abstract

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