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Ion Beam and Plasma Methods of Producing Diamondlike Carbon Films

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ION BEAM AND PLASMA METHODS OF PRODUCING DIAMONDLIKE CARBON FILMS

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SUMMARY

At the NASA Lewis Research Center a variety of plasma and ion beam techniques have been employed to generate diamondlike carbon films. These methods include the use of RF sputtering, DC glow discharge, vacuum arc, plasma gun, ion beam sputtering, and both single and dual ion beam deposition. Since the films have been generated using a wide variety of techniques, the physicochemical properties of these films vary considerably. In general, these films have characteristics that are desirable in a number of applications. For example, the films generated using both single and dual ion beam systems were evaluated for applications including power electronics as insulated gates and protective coatings on transmitting windows. These films were impervious to reagents which dissolve graphitic and polymeric carbon structures. Nuclear reaction and combustion analysis indicated hydrogen to carbon ratios to be 1.00, which allowed the films to have good transmittance not only in the infrared, but also in the visible. Other evaluated properties of these films include band gap, resistivity, adherence, density, microhardness, and intrinsic stress. The results of these studies and those of the other techniques for depositing diamondlike carbon films are presented in this paper.

INTRODUCTION

The deposition of carbon films possessing diamondlike properties has been reported by numerous researchers. A variety of plasma and ion beam techniques have been employed to generate the carbon films. Processes which have been reported to produce diamondlike carbon films include: vacuum evaporation (ref. 1), RF sputtering using inert gas and carbon targets (ref. 2), RF plasma decomposition of hydrocarbon gases (refs. 3 to 6), DC glow discharge of predominantly hydrocarbon gases with a small fraction of argon (ref. 7), coaxial pulsed plasma acceleration using methane gas (ref. 8), vacuum arc using a graphite cathode (ref. 9), ion beam deposition with argon and hydrocarbon scission fragment ions (refs. 10 to 12), and deposition using pure carbon ion beams (ref. 13). Combinations of various techniques have also been utilized such as argon ion bombardment of evaporated carbon films (ref. 14), vacuum carbon arc plasma in conjunction with DC or RF potentials applied to the substrate (ref. 9), and dual ion beam deposition and sputtering techniques (refs. 12,15, and 16).

These diamondlike carbon films may be hard, transparent, chemically inert, electrically insulating, and have been reported to range from amorphous to polycrystalline in structure. Thus they would find wide use in a number of applications, including, power electronics as insulating gates for field effect transistors or as doped semiconductors, protective coatings for optical components, integral coatings for solar cells or laser windows in the infrared, etc. Successful realization of these applications is contingent on effective production of these films, and tailoring their characteristics to meet the needs of the particular application. Therefore, NASA Lewis Research Center has employed a variety of plasma and ion beam methods to generate diamondlike carbon (DLC) films. These methods include the use of RF sputtering with hydrocarbons, DC glow discharge, vacuum arc, coaxial carbon plasma gun, ion beam sputtering, and both single and dual ion beam deposition. This paper presents the process techniques and associated characteristics of the films. Film characteristics include density, hydrogen content, band gap, resistivity, microhardness, dielectric constant, adherence, intrinsic stress, transmittance, and chemical resistance. Some application evaluations will also be presented.

APPARATUS AND PROCEDURE

Diamondlike carbon films were ion beam sputter deposited using an 8 cm diameter source (ref. 17). A 100 eV, 55 mA argon ion beam was produced for sputter cleaning and deposition. An ion beam current density of ~1.0 mA/cm^2 resulted in the vicinity of the sputter target and substrates which were located 20 cm downstream of the ion source. The ion source was operated with a hot filament neutralizer in a vacuum facility which maintained a pressure of 2×10^{-5} torr during operation. The target was made of pyrolytic graphite and films up to 0.15 μm thick were deposited on various substrates.

A 30 cm diameter ion source with its optics masked to 10 cm in diameter was used to directly deposit DLC films (ref. 18). The ion source used argon (Ar) gas in the hollow cathode, located in the main discharge chamber, as well as in the neutralizer. After a discharge was established between the cathode and the anode, methane gas (CH_4) was introduced through a manifold into the discharge chamber. For the depositions reported, the molar ratio of CH_4 to Ar was 0.28. For this system, the total ion beam energy was the sum of the discharge voltage and the screen grid voltage. Typically, current densities were 1 mA/cm^2 at a distance of 2.5 cm axially downstream of the grids. Films were deposited at rates as high as 71 Å/min to film thicknesses as great as 1.5 μm.

It is believed that the amorphous carbon films are produced under conditions where both growth and sputtering occur simultaneously, whereby increased sputtering may decrease the number of graphitic precursors incorporated in the films and hence improve the quality. In addition, Marinow and Dobrew have found that active sites for nucleation are created and the growth and coalescence of the nuclei are enhanced due to an increased mobility of the condensing atoms when film structures are bombarded by inert gas beams (ref. 19). With these factors in mind, a dual beam system was created by adding an 8 cm diameter argon ion source (ref. 18). This system, shown in figure 1, was used to generate another set of DLC films. The 8 cm source, using a filament cathode, was located at a 12° angle with respect to the 30 cm source. This source was used to direct a beam of 200-600 eV argon ions with a current density of 25 μa/cm^2 on the substrate while the deposition from the 30 cm source was occurring.

The plasma gun, shown in figure 2, consisted of two coaxial carbon electrodes (ref. 20). The outer electrode was a hollow cylinder with a large inside diameter along one half of its length and a smaller inside diameter along the other half. The inner electrode was a carbon rod of similar shape, supported by a polytetrafluoroethylene cylinder which centered it within the outer electrode and allowed it to slide axially. To fire the gun, the inner electrode was drawn forward by two solenoids until the two tapered surfaces came into contact. Current was fed into the system creating an arc which caused the resulting plasma to be accelerated forward and deposited onto the substrate. During operation the belljar pressure was ~10^{-6} torr. Voltages of ~1800 V produced currents on the order of 100 kA which resulted in a power level of about 73 MW being dissipated by the gun. One firing event lasted between 0.6 and 0.8 msec.

Figure 3 illustrates a vacuum arc using a graphite cathode to provide a source of high temperature carbon. The cathode, made of spectroscopic grade graphite, was held in a water cooled copper sleeve. A tungsten tipped striker, supplied with current from a 200 A DC welder supply, contacted the cathode and an arc was created. The resulting plasma, consisting of carbon atoms and ions, was accelerated forward through a water cooled copper anode and deposited onto the substrate in a background pressure of 10^{-5} torr.

RESULTS AND DISCUSSION

Compositional characteristics. - Auger analysis of both the single and dual ion beam deposited DLC films showed no evidence of any elements other than carbon and small amounts of argon and oxygen. After argon ion sputtering, 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, and natural diamond are shown in figure 4. The lineshape for the carbon film lies somewhere between those of pyrolytic graphite and diamond. The shoulder in the graphite spectrum at 250 eV is present in the film spectrum, but not so pronounced, whereas natural diamond shows no shoulder. It should also be noted that due to the escape depth of the 270 eV Auger electrons, only the outermost surface layers were sampled in all cases. These would be the most prone to graphitization. Therefore, it was significant that differences between the ion beam deposited film and graphite were observable.

An example of a Secondary Ion Mass Spectroscopy (SIMS) spectrum from a single ion beam deposited DLC film on a silicon substrate is given in figure 5. Note the 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^+, however, Auger analysis indicated no nitrogen. There is a strong H^+ peak at 1 AMU and a cluster of hydrocarbon peaks at 26, 27, 28, and 29 AMU. It is believed that when multiatomic ionic clusters are emitted from the surface, e.g., CH_2^+, these atoms were bound together in the original solid (ref. 21). Therefore it appears likely that the ion beam deposited DLC films contained chemically combined hydrogen.

Nuclear reaction and combustion analysis for hydrogen was also performed on the DLC films (ref. 22). There was a variation in hydrogen content which depended upon the method used for deposition of the DLC film as indicated by the ratios listed in table I. A hydrogen to carbon (H/C) ratio of 0.91 existed for DLC films made by single ion beam deposition. By adding the energy of the second ion source (dual beam) this ratio was reduced to 0.62. Thus, the second source removed some of the hydrogen. The films generated by ion beam sputter deposition from a graphite target had a H/C ratio of 0.22. It has been shown that for the ion beam deposited DLC films, using semiquantitative infrared spectroscopy, the ratio of chemically bonded hydrogen to carbon was between 0.03 and 0.44 (ref. 16). The difference between the two hydrogen analysis techniques indicated the presence of nonbonded hydrogen in the films.

The electron diffraction pattern of the DLC films generated using either single or dual ion beam deposition was found to be characteristic of an amorphous solid. Films deposited by the coaxial carbon plasma gun method were also primarily amorphous as determined by x-ray diffraction.

Optical properties. - The transmittance, reflectance and absorptance of the DLC films on fused silica were obtained using an integrating sphere and the technique described in reference 23. Shown in figure 6(a) is the spectral transmittance for DLC films varying in thickness from 0.08 to 0.33 µm. These films were generated using dual ion beam deposition. Figures 6(b) and 6(c) show the corresponding spectral reflectance and absorptance. At short wavelengths the films all show a large decrease in transmittance while there is a large increase in absorptance. For film thicknesses between 0.08 and 0.15 µm there are only small differences in transmittance at all wavelengths. Increasing the DLC film thickness to 0.33 µm has only a small effect on the transmittance for wavelengths greater than 0.8 µm, but reduces the transmittance to as low as 10 percent at 0.4 µm. Most of this transmittance loss for the 0.33 µm thick film is due to the corresponding increase in absorptance. The thinner films looked clear to yellowlike in appearance, while the thicker DLC film was brown.

The spectral transmittance, reflectance and absorptance for the DLC films obtained from the single ion beam deposition method are similar to those generated using the dual beam source, but have lower spectral transmittance for films greater than 0.12 µm thick. This is evident in figure 7 where the spectral transmittance is shown for DLC films, 0.15 µm thick, generated using both methods. The 0.15 µm thick dual beam film has greater transmittance at all wavelengths when compared to the single beam film of the same thickness. The increased absorption most likely arises from the presence of systems of conjugated double bonds within the film, although the presence of oxygen could play a role. Both the graphitic precursors and oxygen would be expected to be reduced by the increased sputtering from the second source. A dual ion beam deposited DLC film, 0.05 µm thick displays spectral transmittance values greater than 90 percent at wavelengths greater than 0.7 µm. Also shown in figure 7 is the spectral data for an ion beam sputter deposited DLC film 0.17 µm thick. The transmittance was measured only between 0.4 and 0.8 µm for this film, and is very low when compared to the DLC films which were direct deposited. The low transmittance of the sputtered film may be due to its low hydrogen content.

Chemical and physical properties. - A solution of 3 parts H_2SO_4 and 1 part HNO_3 (concentrated acids, by volume) at 80°C was used as the solvent in the chemical dissolution studies. This reagent rapidly dissolves graphitic and polymeric materials, but does not dissolve diamond. Diamondlike carbon films from the single and dual ion beam deposition methods were subjected to the reagent at 80°C for periods up to 20 hr. The films on silicon were unaffected. However, the films on fused silica showed varied behavior. In some cases they were untouched, in others the film was removed from the substrate, but not fully dissolved. These results clearly indicate that the DLC films generated by direct deposition, especially on silicon, were far more resistant to chemical etching than normal polymeric hydrocarbons or graphite.

Scanning transmission electron microscopy (STEM) showed the single and dual ion beam deposited DLC films to be smooth and essentially free of features. No pinholes or other defects were observed. For the vacuum arc and coaxial carbon plasma gun deposited films, STEM showed that particles and inclusions were randomly dispersed throughout the film.

The densities of the DLC films were measured by either the sink or float measurement of flakes or by direct determination of thickness, area and mass. The density of the sputter deposited films was 2.1 g/cm^3, and 1.8 g/cm^3 for the dual ion beam deposited DLC films. The densities were less than either diamond (3.51 g/cm^3) or graphite (2.26 g/cm^3). It is clear from these results that the long range structure of the films was not that of diamond. However, since the films were typically amorphous, one would expect to observe densities much below 2.26 g/cm^3. Therefore, there must be a reasonable fraction of tetragonal bonded carbon. The observed high densities were an indicator of the degree to which the films were diamondlike. The densities were also measured for the DLC films deposited by the other methods and are listed in table I. On the average the densities were 2.0 g/cm^3 for these methods.

The DLC films were deposited on silicon (Si) and intrinsic stress measurements were made using a stress gauge. All of the DLC films exhibited a compressive stress which varied depending on the deposition method. Figure 8 shows that the stress in the CH_4 single beam films can be reduced to values as low as 4×10^9 dyne/cm^2 by decreasing the deposition energy to 90 eV. The compressive stress for an ion beam sputter deposited film was 1.6×10^{10} dyne/cm^2 which was higher than that of direct ion beam deposition, single or dual, with CH_4. Listed in table I are the stress levels for the various DLC films. The data indicates that the film stress does not depend on the hydrogen content, but on other parameters such as deposition technique and conditions.

The adherence of the DLC films on fused silica (SiO_2) was measured following the procedure used by Mirtich (ref. 15). Methane films up to 1.0 μm thick, deposited using either single or dual beam systems, were at least as adherent as the maximum measurable adherence of the adherence tester, namely, 5.5×10^7 N/m^2 or 8000 psi. These films were so adherent that, for some of the films, portions of the SiO_2 gave way with the film still intact. Films which were sputter deposited from a graphite target began to spall at 0.2 μm, indicating an upper limit of allowable thickness of the film. This was expected, since the stress level of this type of film was greater than those made by direct ion beam deposition. A qualitative description of the adherences of the DLC films from the various methods are listed in table I.

Some DLC films deposited by the dual ion beam system on Si have shown no visible signs of deterioration, even after 4 years. However, a film 1.75 μm thick deposited using the single ion beam source spalled within several weeks.

Microhardness was measured by the Vickers diamond indentation method (ref. 24). The DLC films were either single or dual ion beam deposited, vacuum arc or RF sputter deposited on (100) silicon substrates. Figure 9 shows the microhardness as a function of load and thickness for RF sputtered DLC films.

The film hardness increases with decreasing indentor load, and indicates a slight increase with increasing film thickness. The DLC films deposited by the vacuum arc technique had many inclusions, but microhardness data collected from the clear regions indicated a comparable hardness to the RF sputtered films. It was found that the single or dual ion beam deposited DLC films had a hardness half that of diamond.

Electronic properties. - Listed in table I are the values for the optical band gap of the DLC films from the various methods. The DLC films from the single and dual ion beam systems have similar band gaps, but the films which were ion beam sputtered from a graphite target had a higher band gap. Diamondlike carbon films which were RF sputtered or deposited by DC glow discharge had even higher band gaps which were in the range of 1.5 to 3.0 eV. The coaxial carbon plasma gun films had a band gap of ~0 eV, which was indicative of a graphitic (0 eV) as opposed to a diamond (5.0 eV) structure. The differences in the band gaps between the films was most likely due to the difference in hydrogen content of the films.

The resistivity of the various DLC films on silicon was measured and is also listed in table I. Electrical contacts to the film were made with sputtered gold and silver paint. The resistivities for DLC films which were ion beam sputtered, direct ion beam deposited or coaxial carbon plasma gun deposited were all on the order of 10^6 Ω-cm. The DLC films which were RF sputter or DC glow discharge deposited had resistivities in the range of 10^8 to 10^{12} Ω-cm. However, all of the DLC films had resistivities higher than graphite (0.017 Ω-cm), but lower than diamond (10^{14} Ω-cm).

Applications. - Two of the materials most often used as optical windows due to their high transmittance at infrared (IR) wavelengths are zinc selenide (ZnSe) and zinc sulfide (ZnS). However, these materials are soft and often degrade when subjected to a particle-impacting environment (ref. 25). DLC films have the potential to protect these window materials from rain and particle erosion as well as chemical attack. Therefore, DLC films were ion beam sputter deposited and also direct deposited with either the single or dual ion beam on ZnS and ZnSe. The DLC coated window surfaces were then exposed to aluminum oxide (Al_2O_3) particles in a microsandblaster, and water droplets at speeds up to 400 mph.

In order to improve the adherence of the DLC films on ZnS and ZnSe, a thin intermediate coating of germanium (Ge) was used prior to deposition of the DLC films (ref. 26). Ion implantation of the ZnS and ZnSe surfaces with helium (He) at energies of 100 keV and at doses to 2×10^{17} particles/cm^2 prior to the deposition of the DLC/Ge film also helped to improve the adherence but as a bonus improved the physical hardness of the substrate. The DLC films plus an intermediate coating of 0.05 μm Ge deposited on the window materials and also windows He ion implanted showed adherence values equal to the strength of the substrate.

A spectrophotometer was used to measure the IR transmittance of the DLC films deposited on the ZnS and ZnSe substrates. For the DLC films, 0.1 μm thick, deposited on ZnS or ZnSe and measured between 2.5 and 25 μm, the spectral transmittance of the material did not change in this wavelength region. The use of an intermediate Ge coating or ion implantation also did not seem to alter the IR transmittance of the ZnS and ZnSe. Shown in figure 10 is the IR specular transmittance of a ZnSe substrate coated with a 0.1 µm thick DLC film from the single beam plus an intermediate layer of 0.03 µm Ge along with the transmittance of an uncoated ZnSe. Although there is a reduction in the IR specular transmittance due to the DLC/Ge film at shorter wavelengths, only a 1 percent loss occurs at 10 µm.

In order to determine the protection the DLC films afforded the ZnS and ZnSe, the surfaces were first exposed to 27-µm-diam Al_2O_3 particles with an estimated stream velocity of 1100 ft/sec in a microsandblaster (ref. 27). The protective quality of the film was then characterized by the change in specular transmittance due to the particle erosion with the Perkin-Elmer spectrophotometer between 2.5 and 50 µm. Figure 11 indicates the change in specular transmittance at 10 µm due to total erosion time for various surfaces of ZnS coated with the DLC/Ge films. In the figure there is an envelope which portrays the erosion rate of the uncoated surface, which is necessary because each ZnS substrate had a slightly different initial transmittance due to the substrate thickness. As the figure indicates, neither the DLC/Ge films or ion implantation plus the DLC/Ge films afforded the ZnS surfaces any extension in particle erosion lifetime after exposure to the Al_2O_3 particles. The same was true for the ZnSe surfaces.

The ZnS surfaces were also evaluated for rain erosion performance at Wright Patterson Air Force Base. The rain erosion facility consisted of a rotating arm apparatus with speeds to 470 mph and a simulated rainfall of 1 in./hr. Zinc sulfide, DLC/Ge coated ZnS, and ZnS first implanted with He ions at doses to 2×10^{17} particles/cm^2 and then coated with the DLC/Ge films were subjected to the rain erosion. It was apparent from optically viewing the ZnS surfaces exposed to the water droplets at 400 mph, that there was an improvement in the performance in the ZnS surface which was ion implanted and coated with a 0.1 µm DLC film from the single beam plus an intermediate layer of 0.04 µm Ge. The ion implantation plus the DLC/Ge coating resulted in a decrease in the number of new pits in the ZnS surface, and an increase in resistance to the formation of subsurface ring fractures. This could be expected since the ion implantation improved the physical hardness at the surface to a depth of ~1.0 µm of the ZnS (ref. 26). There were no changes in the IR specular transmittance for the ZnS surface ion implanted and DLC/Ge coated after exposure to the rain erosion.

Although He ion implantation plus a DLC/Ge film did not afford any protection to the ZnS and ZnSe windows exposed to the simulated particle erosion, it did however, improve the performance of ZnS exposed to rain erosion. Hardening of the window surface by ion implantation plus the addition of a thick stress-free DLC film, may be a surface which would protect, thereby increasing the lifetime of infrared transmitting windows from both rain and less severe particle erosion.

A systematic attempt to study the electrical characteristics of the DLC films on compound semiconductors and to explore their potential as a gate dielectric for insulated-gate technology for very high (1 to 100 GHz) speed integrated circuits was also performed (ref. 28). The DLC films were direct deposited on indium phosphide (InP), gallium arsenide (GaAs), and Si semiconductor wafers to evaluate their potential as a new electronic material in a metal-insulator (carbon)-semiconductor (MIS) device configuration for solid state power devices for space applications.

After directly depositing the DLC films, using both single and dual ion beams, on the p-type wafers, circular 0.5 μm aluminum (Al) gate electrodes were deposited on the DLC films from a resistance heated boat at 10^{-6} torr to form the MIS system. Ohmic contacts were formed by depositing 0.5 μm Al on the Si back surface and 0.5 μm 5 percent Au-Zn alloy on the InP and GaAs back surfaces. The contact metalization was then sintered at 375° C for 5 min. in forming gas.

The fixed insulator charge number density of the MIS system was evaluated by high frequency 1 MHz capacitance-voltage C-V measurements. The analysis of the C-V data is shown in figure 12 for DLC films on InP, Si, and GaAs substrates. This figure displays the variation of fixed insulator charge number density as a function of the ion beam energy at which the DLC film was deposited on the substrates. The lower x-axis shows the energy of the single ion beam system, while the upper x-axis shows the energy of the dual ion beam system. The results show that the fixed insulator charge number density increases with ion beam deposition energy for all of the InP, GaAs, and Si substrates.

Analysis of the quasistatic C-V data yielded a U-shaped distribution of interface state density for InP, GaAs, and Si substrates. Figure 13 shows the minimum interface state density in the middle of the band gap of the substrate as a function of ion beam energy of the deposition source. The lower and the upper x-axis are the same as in figure 12. The interface state density as a function of ion beam deposition energy increases dramatically for DLC films deposited on GaAs, increases slightly for DLC films deposited on InP, and remains essentially unchanged for DLC films deposited on Si substrates.

Diamondlike carbon films do not appear to be a promising new electronic material as a gate dielectric for insulated-gate technology for application in microelectronics. This is due to low optical band gaps, low resistivity, very high fixed insulator charge number density, and high interface state density. In addition, these films generally decomposed at temperatures above 450° C, and therefore are not suitable for use in microelectronics processing.

CONCLUSIONS

A variety of plasma and ion beam methods were employed to generate diamondlike carbon films. These methods included RF sputtering, DC glow discharge, vacuum arc, coaxial carbon plasma gun, ion beam sputtering, and both single and dual ion beam deposition. Auger analysis of the single and dual ion beam deposited DLC films showed no evidence of any elements other than carbon and small amounts of argon and oxygen. SIMS analysis indicated that these ion beam deposited DLC films contained chemically combined hydrogen. Nuclear reaction and combustion analysis for hydrogen showed there was a variation in hydrogen content which depended upon the method used for deposition of the DLC film. A hydrogen to carbon ratio of nearly one existed for single ion beam deposited films, while the ratio was reduced to 0.62 for the dual ion beam films. Films generated by ion beam or RF sputtering though, had low H/C ratios. The spectral transmittance for DLC films obtained from the single ion beam deposition method was similar to those generated using the dual beam source, whereas, the spectral transmittance of the ion beam sputtered DLC films was much lower than the direct deposited films. The low transmittance of the sputtered films may be due to its low hydrogen content. Electron and x-ray diffraction patterns were found to be characteristic of an amorphous solid for DLC films either single or dual ion beam deposited, and for those films which were plasma gun deposited.

Diamondlike carbon films from the single or dual ion beam deposition methods were impervious to reagents which dissolve graphitic and polymeric materials. These direct deposited films were also smooth and free of pinholes or other defects as determined by STEM. For the vacuum arc and plasma gun DLC films though, STEM showed that particles and inclusions were randomly dispersed throughout the films. The densities of the various DLC films were less than either diamond or graphite, therefore indicating that the long range structure of the films was not that of diamond. The ion beam sputtered and deposited films both exhibited a compressive stress, which did not depend on hydrogen content, but on other parameters such as deposition technique and conditions. The adherence of most of the DLC films was very good, but the films generated by the vacuum arc and plasma gun had poor adherences which was most likely due to the poor surface quality of these films. The microhardness of the RF sputtered and vacuum arc DLC films was comparable, but lower than the direct deposited films. All of the microhardness values were lower than diamond. The band gaps for the single and dual ion beam deposited DLC films were similar, while the RF sputtered, DC glow discharge, and ion beam sputtered films had band gaps which were higher. The coaxial carbon plasma gun DLC films had a band gap of ~0 eV which was indicative of a graphitic structure. The DLC films had similar resistivities with the RF sputtered and DC glow discharge films somewhat higher, but all still lower than the resistivity of diamond.

Although the physico-chemical properties of the DLC films varied, the films in general had characteristics which were desirable for certain applications. Therefore, the DLC films were evaluated as protective coatings for optical windows, and as a gate dielectric for insulated-gate technology. The DLC film did not afford any protection to the infrared windows exposed to simulated particle erosion, however, they improved the performance of ZnS exposed to rain erosion. Therefore, a thick stress-free DLC film may have the potential to increase the lifetime of an IR transmitting window. In the second application evaluation the DLC films were found to be deficient in electrical properties conducive to microelectronics. It can be seen from the properties, as well as the advantages and disadvantages of each DLC film deposition technique, there is the potential to tailor the characteristics of the DLC film to meet the needs of a particular application.

REFERENCES

1. J. Kakinoki, K. Katada, T. Hanawa, and T. Ino; Acta Crystallogr. Sect. A, **13**, pt. 3, 171-179 (1960).

2. Z. Marinkovic and R. Ray, Carbon, **14**, 329-331 (1976).

3. R.T. Gambino and J.A. Thompson, Solid State Commun., **34** 15-18 (1980).

4. L. Holland and S.M. Ojha, Thin Solid Films, **48**, L21-L23 (1978).

5. S.M. Ojha, H. Norstrom, and D. McCulluch, Thin Solid Films, **60**, 213-225 (1979).

6. L.P. Anderson, S. Berg, H. Norstrom, and R. Olaison, Thin Solid Films, **63**, 155-160 (1979).

7. D.S. Whitmell and R. Williamson, Thin Solid Films, **35**, 255-261 (1976).

8. M. Sokoliwski, A. Sokolowska, A. Michalski, Z. Romanowski, A. Rusek-Mazurek, and M. Wronikowski, Thin Solid Films, **80**, 249-254 (1981).

9. V.E. Strel'nitskii, V.G. Padalka, and S.I. Vakula, Zh. Tekh. Fiz., **48**, 377-381 (1978).

10. S. Aisenberg and R. Chabot, J. Appl. Phys., **42**, 2953 (1971).

11. T.J. Moravec and T.W. Orient, J. Vac. Sci. Technol., **18**, 226-228 (1981).

12. C. Weissmantel, J. Vac. Sci. Technol., **18**, 179-185 (1981).

13. I.I. Aksenov, S.I. Vakula, V.G. Padalka, V.E. Strel'nitskii, and V.M. Khoroshikh, Sov. Phys. Tech. Phys., **25**, 1164-1166 (1980).

14. S. Fujimori and K. Nagai, Jpn. J. of Appl. Phys., **20**, L194-L196 (1981).

15. M.J. Mirtich, J. Vac. Sci. Technol, **18**, 186-189 (1981).

16. J.C. Angus, M.J. Mirtich, and E.G. Wintucky, Metastable Materials Formation in Ion Implantation, S. Picraux and W. Choyke, eds., Proc. Materials Res. Soc. Meeting, Boston, MA, 433 (1981).

17. B.A. Banks and S.K. Rutledge, NASA TM-82873 (1982).

18. M.J. Mirtich, D.M. Swec, and J.C. Angus, NASA TM-83743 (1984).

19. M. Marinov and D. Dobrev, Thin Solid Films, **42** 267-268 (1977).

20. D.M. Sater, D.A. Gulino, and S.K. Rutledge, NASA TM-83600 (1984).

21. A. Benninghoven, Surf. Sci., **53**, 596-625 (1975).

22. J.C. Angus, J.E. Stultz, J.R. MacDonald, M.J. Mirtich, S. Domitz, and P.J. Shiller, Thin Solid Films, **118**, 311-320 (1984).

23. R.L. Bowman, M.J. Mirtich, and A.J. Weigand, NASA TMX-52687 (1969).

24. J.C. Kolecki, NASA TM-82980 (1982).

25. M.J. Mirtich, D. Nir, D.M. Swec, and B.A. Banks, NASA TM-87083 (1985).

26. M.J. Mirtich, D. Nir, D.M. Swec, and B.A. Banks, J. Vac. Sci. Technol. A, **4**, 2680-2681 (1986).

27. D.M. Swec, M.J. Mirtich, D. Nir, and B.A. Banks, J. Vac. Sci. Technol. A, **4**, 3030-3031 (1986).

28. V.J. Kapoor, M.J. Mirtich, and B.A. Banks, J. Vac. Sci. Technol. A, **4**, 1013-1017 (1986).

TABLE I. - EVALUATION OF DIAMONDLIKE CARBON FILM DEPOSITION TECHNIQUES

Property	Deposition technique						
	Ion beam sputter	Single ion beam	Dual ion beam	Vacuum arc	RF sputter	dc Glow discharge	Plama Gun
Adherence	Very good	Very good	Very good	Very poor	Good	Good	Poor
H/C ratio	0.22	0.91	0.62	low	----------	----------	----------
Density, g/cm^3	2.1	1.8	1.8	2.75	1.5 to 2.0	1.8	----------
Band gap, eV	0.909	0.382	0.343	----------	1.5 to 3.0	1.5 to 2.0	0
Stress, dyne/cm^2	1.6×10^{10}	0.9×10^{10}	0.9×10^{10}	----------	----------	----------	----------
Microhardness, kg/mm^2	----------	5000	5000	1050	1050	----------	----------
Resistivity, ohm-cm	5.29×10^6	8.66×10^6	3.35×10^6	----------	10^8 to 10^{12}	$10^8\times10^{11}$	1.2×10^6
Deposition rate, Å/min	20	60	60	~10,000	~1000	~600	~200
Major advantages	Uniform films, good adhesion	Uniform films, good adhesion	Uniform films, good adhesion	Rapid deposition rate	Uniform films, simplicity	Simplicity	Potential H_2 control
Major disadvantages	Low deposition rate	Low deposition rate	Low deposition rate	Inclusions	Poor adhesion on metals	Nonuniform films	Inclusions

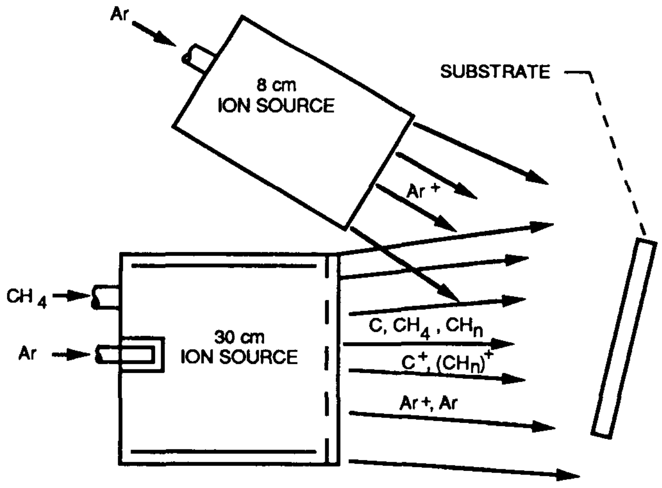
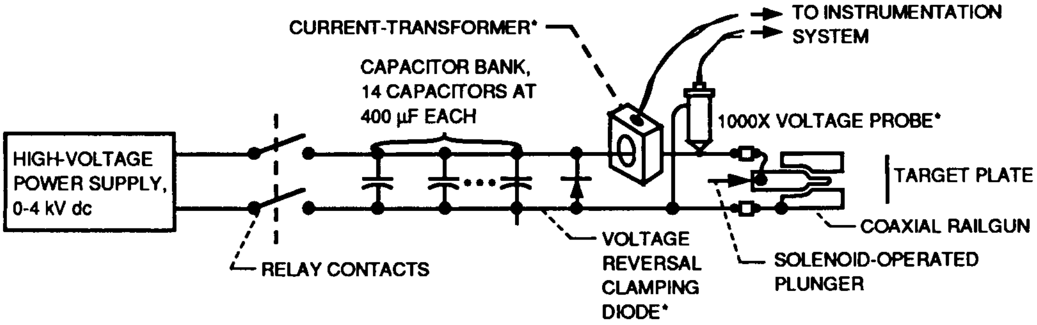


Figure 1. - Schematic of dual ion beam deposition system.



* THESE COMPONENTS WERE CONTAINED WITHIN THE BUSBAR ASSEMBLY, WHICH IS NOT EXPLICITLY SHOWN IN THIS SCHEMATIC.

Figure 2. - Basic elements of coaxial carbon plasma gun deposition system.

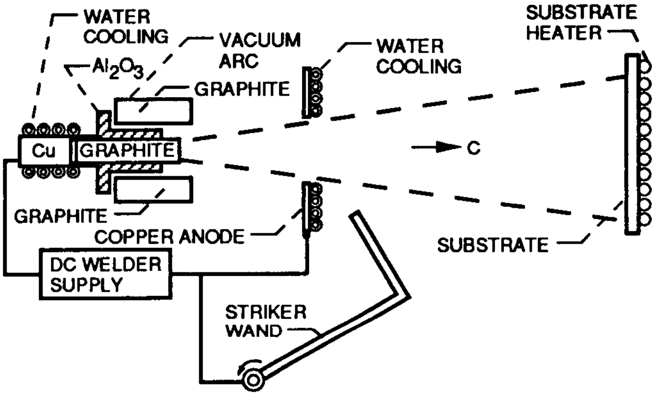


Figure 3. - Vacuum arc deposition system.

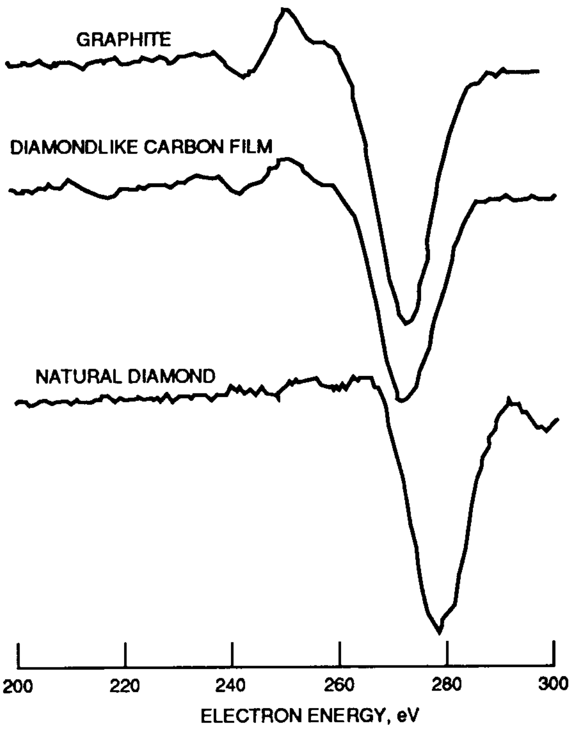


Figure 4. - Auger spectra of pyrolytic graphite, a single ion beam deposited DLC film, and natural diamond.

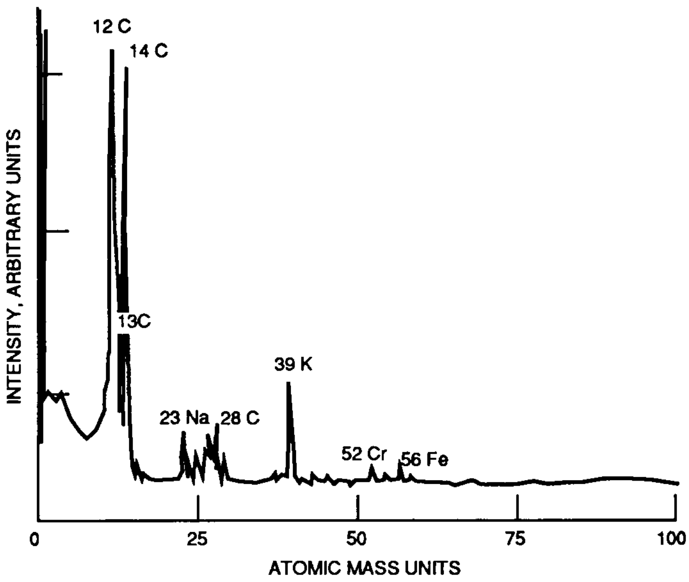
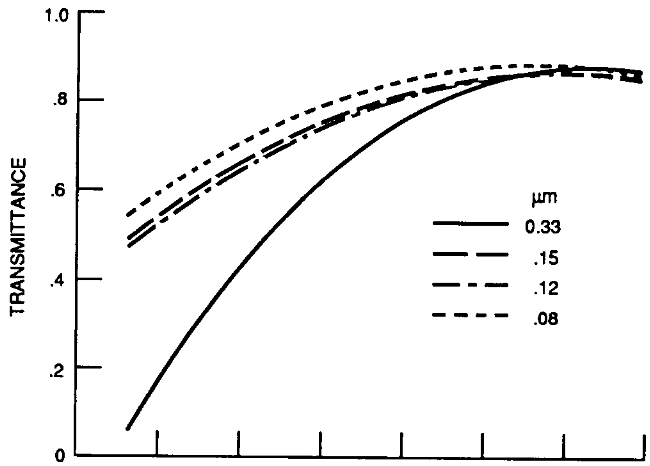
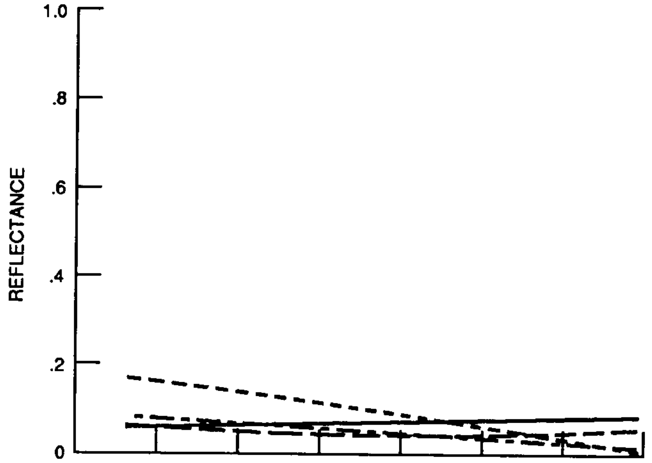


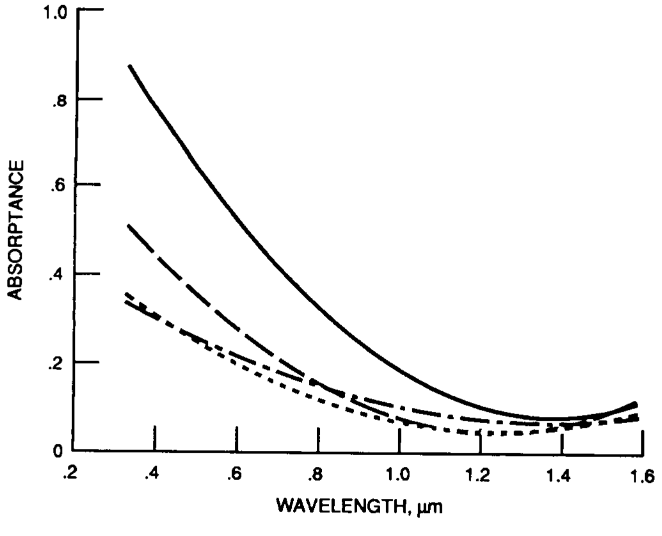
Figure 5. - Secondary ion mass spectrum of a DLC film from the single ion beam deposition system.



(a) TRANSMITTANCE.



(b) REFLECTANCE.



(c) ABSORPTANCE.

Figure 6. - Transmittance, reflectance and absorptance as a function of wavelength for various thicknesses of DLC films from the dual ion beam deposition system.

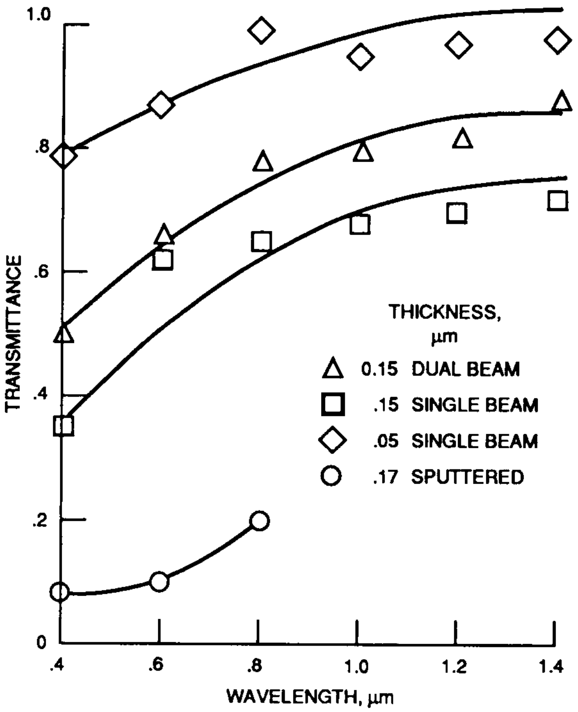


Figure 7. - Transmittance as a function of wavelength for DLC films deposited with the single or dual ion beam system and sputtered from a graphite target.

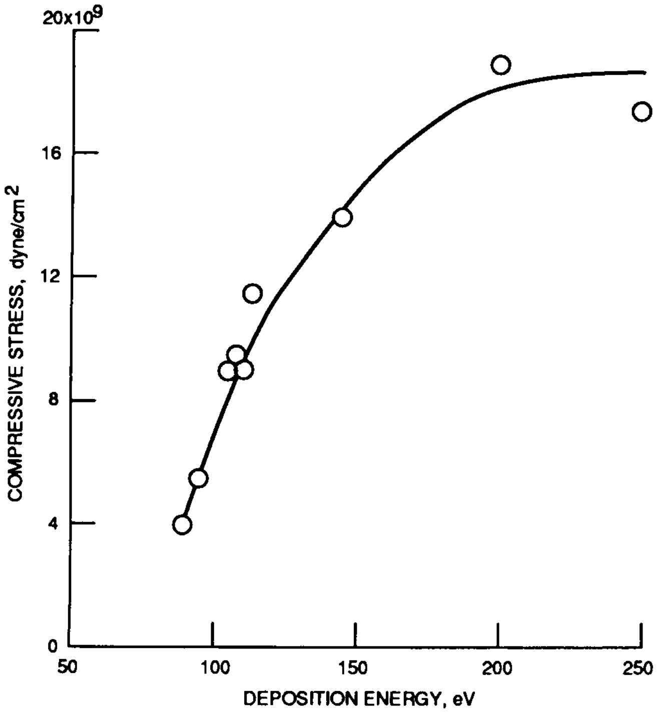


Figure 8. - Compressive stress as a function of deposition energy for DLC films from the single ion beam deposition system.

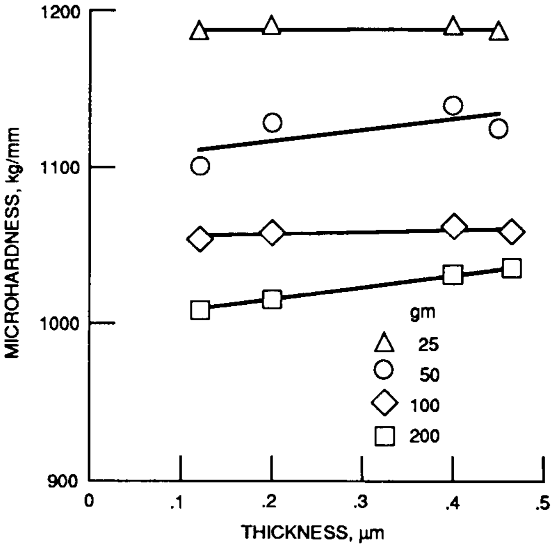


Figure 9. - Microhardness as a function of film thickness and load for DLC films RF sputter deposited.

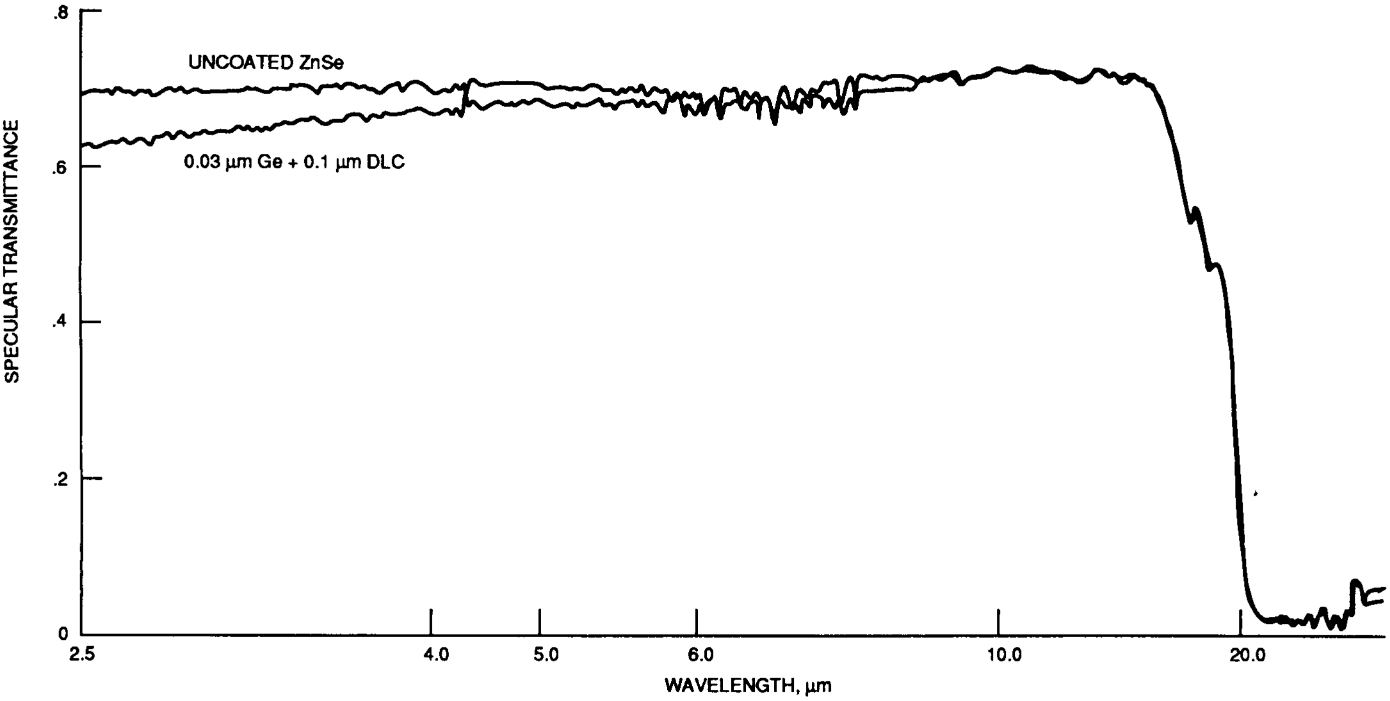


Figure 10. - Specular transmittance of a DLC film from the single ion beam deposition system plus an intermediate layer of Ge on ZnSe and uncoated ZnSe.

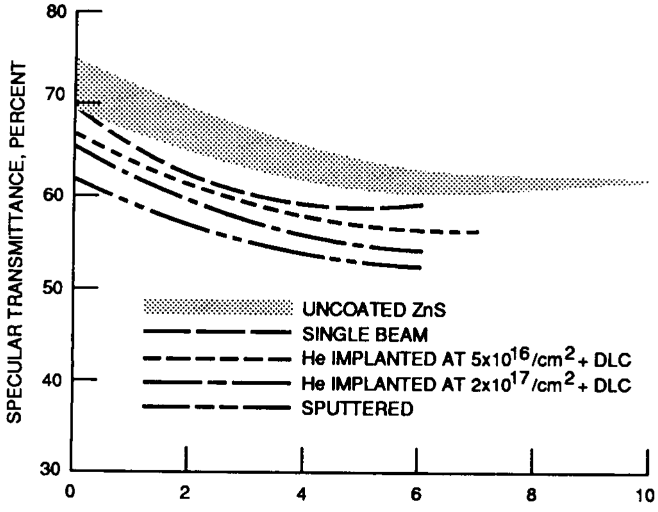


Figure 11. - Change in specular transmittance at 10 μm due to total erosion time for various surfaces of ZnS coated with DLC/Ge films.

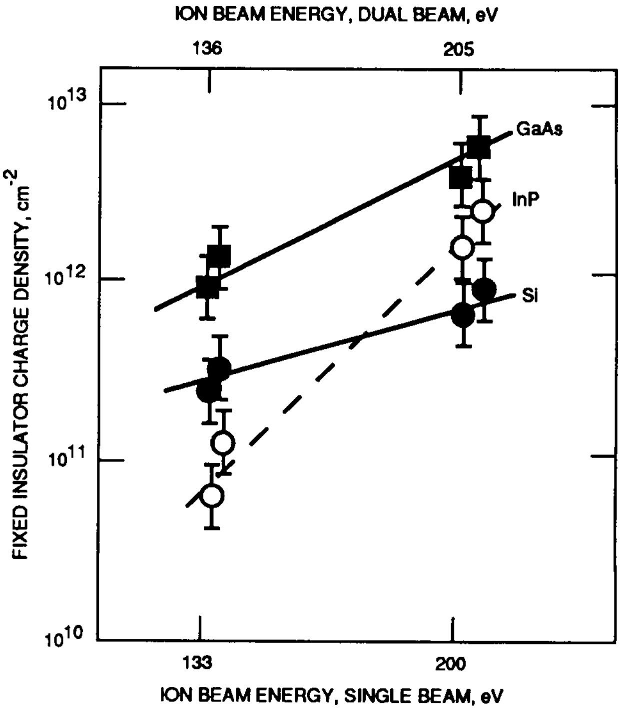


Figure 12. - Variation of the fixed insulator charge number density as a function of ion beam deposition energy for DLC films on GaAs, InP, and Si.

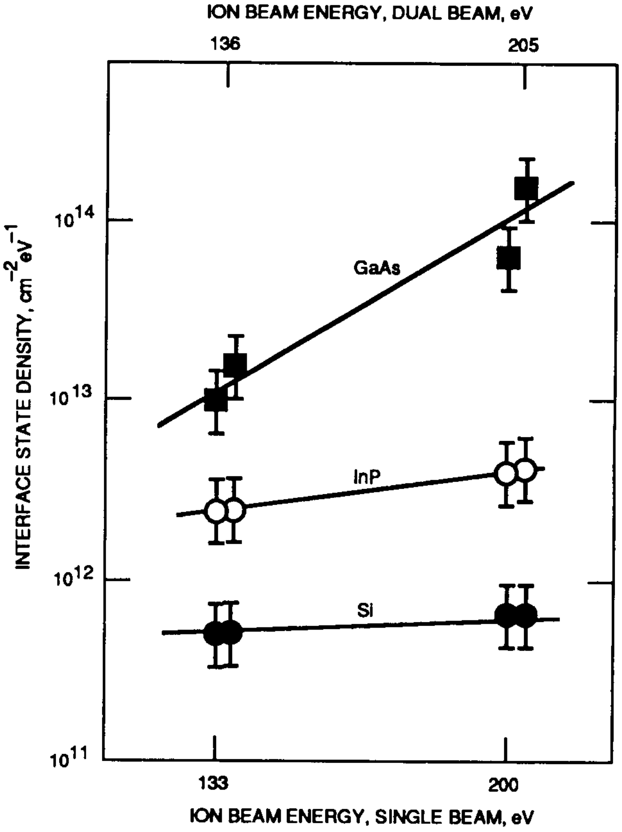


Figure 13. - Variation of the interface state density as a function of ion beam deposition energy for DLC films on GaAs, InP and Si.

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16. Abstract

At the NASA Lewis Research Center a variety of plasma and ion beam techniques have been employed to generate diamondlike carbon films. These methods include the use of RF sputtering, DC glow discharge, vacuum arc, plasma gun, ion beam sputtering, and both single and dual ion beam deposition. Since the films have been generated using a wide variety of techniques, the physico-chemical properties of these films vary considerably. In general, these films have characteristics that are desirable in a number of applications. For example, the films generated using both single and dual ion beam systems were evaluated for applications including power electronics as insulated gates and protective coatings on transmitting windows. These films were impervious to reagents which dissolve graphitic and polymeric carbon structures. Nuclear reaction and combustion analysis indicated hydrogen to carbon ratios to be 1.00, which allowed the films to have good transmittance not only in the infrared, but also in the visible. Other evaluated properties of these films include band gap, resistivity, adherence, density, microhardness, and intrinsic stress. The results of these studies and those of the other techniques for depositing diamondlike carbon films are presented in this paper.

17. Key Words (Suggested by Author(s)) Diamondlike carbon films Ion beam and plasma deposition	18. Distribution Statement Unclassified – Unlimited Subject Category 27

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