Optical properties of amorphous C/diamond thin films

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Amorphous C/diamond films have been prepared by rf plasma enhanced vapor deposition from a CH_4/Ar gas mixture. Infrared and optical-ultraviolet absorption characteristics are reported and used to characterize the bonding and optical properties of these films. It has been found that the optical band gap is not related to the hydrogen content in the films and varies according to the dc self bias developed during deposition. The IR data show that the hydrogen in the α -C/diamond films is associated with triply bonded sp^1 carbon as in acetylene. The optical band gap of the films can be varied from 1.2–4.0 eV.

INTRODUCTION

In recent years amorphous semiconductors have been studied extensively for the fabrication of electronic and photovoltaic devices. Due to large area deposition capabilities and the possibility of deposition on a variety of surfaces this relatively inexpensive amorphous material technology has attracted much attention.

Diamondlike carbon has been studied as an amorphous material with technological potential since it was shown that these films could be deposited using a chemical vapor deposition (CVD) process.¹ Diamondlike carbon, α -C, α -C:H, ion-beam deposited carbon, α -C/diamond all refer to a material that contains varying amounts of the three allotropes of carbon. Namely diamond (sp^3 bonds), graphite (sp^2) and carbyne (sp^1). Large band gap, extreme hardness, chemical inertness, optical transparency over a wide range of wavelengths, good thermal conduction, and electrically insulating characteristics are some of the properties that make amorphous carbon a technologically attractive material. These diamondlike carbon films have been deposited in a variety of ways. These include CVD (microwave,² rf,¹ and dc³), ion beam deposition⁴ and vacuum arc deposition.⁵

α -C/diamond films are a form of diamondlike films which contain diamond crystallites, surrounded by a matrix of amorphous carbon.^{6,7} These diamond crystals have dimensions of 20–200 nm and are seen in clusters in the α -C/diamond films. Scanning electron microscopy (SEM) shows these films to be pinhole free, but with a large compressive stress that is in the GPa range.⁸ Electronic characterization has shown the films to have resistivities in the range of 10^6 – $10^8 \Omega \text{ cm}$.⁹ The major advantage of α -C/diamond films compared to the more pure polycrystalline diamond films are that they can be deposited on substrates kept at room temperature. Hence they are suitable as a coating which has significant diamond content for materials such as polymers.

In this work we investigate the optical absorption properties of α -C/diamond films. It is found that the optical band gap of these films can be changed by over a factor of three, by varying the deposition conditions. The depo-

sition parameter which is found to be significant in determining the optical band gap is the dc self-bias voltage in the rf plasma. The relationship between the optical band gap, dc self-bias and the hydrogen content is investigated. It is found that the hydrogen content is not directly related to the optical band gap. The experimental results are more in keeping with a change in the microstructure of the films with varying dc bias as predicted by the subplantation model.¹⁰

EXPERIMENT

The films studied were deposited using rf plasma enhanced CVD. In this method a CH_4/Ar gas mixture is broken down into C^+ ions and CH radicals in a predominantly Ar plasma by a capacitively coupled 13.56 MHz rf power generator. The sample which is placed on the lower electrode is kept at 20 °C by a feedback controlled cooling system. Substrates used were {100} n -type Si wafers of 5–10 $\Omega \text{ cm}$ resistivity. Before deposition, substrates were degreased and then subjected to a 20 s preclean in an Ar^+ ion plasma. The preclean was long enough to remove any native oxide on the Si, while minimizing damage to the Si surface. All depositions were performed at a pressure of 300 mTorr. Deposition times for the α -C/diamond films were varied from 5–10 min.

For the first set of experiments, the CH_4 to Ar ratio was kept at 8%, with the dc self-bias developed in the rf plasma enhanced CVD method, varied by adjusting the rf power. The dc self bias voltage which is developed between the plasma and the electrodes, gives rise to an electric field which accelerates ions from the plasma onto the electrode. Hence the energies of the ions taking part in film growth on the substrates, which are placed on the lower driven electrode, is closely related to the dc self bias voltage. Optical absorption measurements were performed using a Perkin Elmer Lambda 9 UV-VIS-IR spectrophotometer. The sample preparation and machine setup are explained elsewhere.¹¹ In the second set of experiments, the dc self bias voltage was kept at approximately –400 V, while the CH_4 -to-Ar ratio was varied between 0.1% and 8%. Infrared (IR) measurements were performed using a Fourier

FIG. 1. Free standing *a*-C/diamond membrane used for spectrophotometry experiments.

transform Bruker spectrometer in the reflection mode. IR data were calibrated against a Si sample.

The samples used for optical-UV (ultraviolet) spectrophotometry were free standing *a*-C/diamond membranes that were supported on a Si frame. The sample dimensions were of the order of $100 \mu\text{m}^2$ in area (Fig. 1). Membrane dimensions are limited by the film thickness and compressive stress present in the film.

RESULTS

Normalized optical transmission data together with the Tauc plots are given in Fig. 2. The figures show that an optical band gap variation from 1.2–4.0 eV can be achieved by varying the dc self-bias voltage across the electrodes. An optical band gap of 4 eV seems to indicate that under these deposition conditions the *a*-C/diamond films obtained, are optically similar to type I crystalline diamond.

In past work it was thought that the hydrogen in the films, always present in some finite quantity due to the use of a hydrocarbon source gas, influences the optical properties.^{12–14} It was shown that the optical band gap decreased with an increase of hydrogen in the films. The decrease in hydrogen in turn was thought to be related to the increase in dc bias voltages in the plasma. The prevalent model based on this view is that an increase in the dc bias voltage leads to the growing film being exposed to more energetic ion bombardment, and that this gives rise to the removal of weakly bonded hydrogen in the films.¹³ The model further suggests that more sp^3 bonds will be present in films deposited at a higher dc bias.

Table I shows the tabulated IR peaks for the data shown in Figs. 3 and 4. Examination of the IR data gives some interesting information regarding the hydrogen content and the structure of the amorphous C in the films. Table II gives optical data derived from spectrophotometry and ellipsometry. Table III also shows the variation in the hydrogen content of the *a*-C/diamond film with CH_4 -to-Ar ratio.

FIG. 2. Normalized transmission data vs energy, and Tauc plots for films deposited at various dc bias voltages.

DISCUSSION

Figure 3 shows that the peak centered around $\sim 3300 \text{ cm}^{-1}$ gets stronger and more distinct as the dc self bias is increased. The spectra for the films deposited at low dc biases have an extra band centered around 3420 cm^{-1} . This peak cannot be assigned to any known IR vibration as yet. Stenzel *et al.*¹⁵ also saw an absorption near 3400 cm^{-1} when they were looking at the IR absorption spectra

TABLE I. IR peak assignment for *a*-C/diamond films.

Wave number/cm ⁻¹	Assignment
3420	unassigned
~3300	—C≡C—H <i>sp</i> ¹
3080	CH ₂ (olefinic) <i>sp</i> ²
~3010	CH(olefinic) <i>sp</i> ²
2960	CH ₃ (asymm) <i>sp</i> ³
2360 ⁺ /—30	O=C=O due to path difference
1592	C=C aromatic stretch <i>sp</i> ²
1568	C=C aromatic stretch <i>sp</i> ²
1493	C=C aromatic stretch <i>sp</i> ²
1430	—CH ₃ or >CH ₂
1352	amorphous carbon
1280	CH ₂ (out-of-plane) <i>sp</i> ²
1205	C—H aromatic ring (out-of-plane)
1167	microcrystalline/amorphous diamond
1064	C—H aromatic ring (out-of-plane)
990	—CH=CH ₂
780	C—H aromatic ring (out-of-plane)

of *a*-C:H, and concluded that this band was due to oxygen and/or nitrogen contaminants. Applying the method used by Fujimoto *et al.*,¹⁶ the relative hydrogen content for these films was determined and the results are tabulated in Table II. DC81, with the highest H content is taken as having a relative H content of 100%.

The IR spectra in Figs. 3 and 4, indicate that the majority of the hydrogen in the *a*-C/diamond films is triple bonded *sp*¹ carbon as in acetylene. There does not seem to be any correlation between the triple bonded C—H content and the optical band gap variation obtained from the data in Fig. 2, and shown in Table II. Direct and indirect band gap measurements appearing in Table II have been calculated by plotting $(\alpha)^2$ vs $h\nu$, and $(\alpha)^{1/2}$ vs $h\nu$, respectively; α being the absorption coefficient of the *a*-C/diamond film. These are the standard methods used in measuring the optical band gap for direct and indirect semiconducting materials. It is interesting to note that the band gap values obtained from the intercept of the Tauc plot, the standard method for amorphous materials, closely follows the values obtained by considering *a*-C/diamond to be an indirect band gap material.

The very strong IR absorption at 3225 cm⁻¹ is consistent with that observed for hydrogen bonded to *sp*¹ carbon, the carbon forming a triple bond with another carbon as in acetylene (H—C≡C—H). This could be interpreted in

TABLE II. Optical data for *a*-C/diamond films with varying dc self bias voltage.

Sample	dc82	dc61	dc80	dc62	dc63	dc81
Thickness/Å	780	690	800	570	420	200
Refractive index	2.0	2.1	2.2	2.1	2.1	2.5
Deposition voltage/V	-70	-160	-265	-320	-400	-500
Absorption edge/eV	1.25	1.25	4.0	2.5	3.0	2.0
Tauc intercept/eV	1.21	1.22	4.0	2.2	2.84	1.8
Relative H content	6%	3%	5%	19%	26%	100%
Direct band gap/eV	1.26	1.30	4.05	2.76	2.94	2.16
Indirect band gap/eV	1.22	1.20	3.94	2.11	2.81	1.8

TABLE III. Optical data for *a*-C/diamond films with varying CH₄-to-Ar ratios.

Sample	dc114	dc115	dc116	dc117	dc119	dc118	dc128
CH ₄ :Ar ratio	0.1%	0.5%	1.0%	2.0%	3.0%	4.0%	8.0%
Thickness/Å	150	150	100	100	140	160	400
Refractive index	2.3	2.4	2.4	2.7	2.4	2.6	2.2
Deposition voltage/V	-425	-375	-400	-400	-400	-375	-425
Relative H content	81%	62%	68%	100%	83%	82%	26%

two ways. One possible interpretation is that these are acetylenelike carbon chains in the films consistent with the presence of an intermediate "carbyne" phase between graphite and diamond.¹⁷ The existence of such a carbon phase has been challenged by Smith and Buseck,¹⁸ who attributed the observed diffraction data to mineral impurities in the samples analyzed. We have also found some evidence of a nongraphitic hexagonal phase in the plasma deposited films which are free from mineral impurities. These hexagonal structures can be ascribed to carbynes.¹⁹ However, it is still unclear as to how acetylenelike carbon chains arrange themselves to give a hexagonal unit cell structure. An alternative view is that the films have acetylene incorporated from the gas phase as it is thought to be the stable byproduct remaining from CH₄ plasma decomposition.²⁰ Either way the results confirm the incorporation of triple bonded *sp*¹ carbon.

FIG. 3. IR data plot of absorption (arb. units) vs wave number for *a*-C/diamond films deposited at various dc bias voltages.

FIG. 4. IR data plots of absorption (arb. units) vs wave number for *a*-C/diamond films deposited with varying CH₄:Ar ratios.

The reason for a maximum hydrogen content seen in the film deposited at a maximum dc self-bias in Fig. 3 is not clear, and is not in accordance with the existing simple model. The film with the lowest relative H content of 3%, dc61 (−160 V) has a relatively low optical band gap of approximately 1.2 eV. However, the film dc80 (−265 V) has a band gap of 4 eV and a relative H content of 5%. Further increases in the dc bias voltage during deposition result in an increase in the H content and a lowering of the optical band gap. This suggests that the role of the dc bias during deposition is not simply to alter the properties of the C films by altering the H content within them. Rather, there seems to be a narrow window between −160 V and −265 V dc bias, for the particular deposition parameters of pressure, CH₄:Ar content and the temperature used, which influences the structure of the film to give a dramatic increase in the optical band gap from 1.2 to 4 eV. Note that comparing films dc80 and dc62 deposited at −265 V and −320 V, the relative H content rises from 5% to 19%, but the optical band gap reduces from 4 to 2 eV.

Khan *et al.*²¹ too, did not see a systematic variation in the optical properties of their films with hydrogen content. One reason for there being no correlation between the optical properties and the hydrogen content could be due to the structural components that constitute our films. In the

FIG. 5. Characteristic IR spectrum of *a*-C/diamond films.

a-C/diamond films studied here, the amorphous component is not a mixture of *sp*² and *sp*³ bonded C, but rather, predominantly *sp*¹ carbyne hybridizations, as suggested by the IR data.

The IR spectra in Fig. 5 is typical of the *a*-C/diamond films. All the IR spectra appearing in Figs. 3 and 4, show a similar appearance in this fingerprint region. This signature of *a*-C/diamond films is dominated by C—H aromatic absorptions. Two of the peaks appearing are assigned to the Raman microcrystalline/amorphous diamond and amorphous carbon vibrations. Table I gives the assignments of the peaks appearing in Fig. 5.

Absorption peaks appearing in Fig. 5 at 1205, 1064, and 780 cm^{−1} are attributed to out-of-plane aromatic C—H bending modes. Peaks at 1592, 1568, and 1493 cm^{−1} are assigned to aromatic C=C stretches. Stretching modes characteristic of *sp*² hybridized CH₂ groups give rise to absorptions at 3080 and ~3010 cm^{−1}; bending vibrations of the groups produce absorptions at 1280 and 990 cm^{−1}. CH₃ groups with *sp*³ hybridization give rise to an asymmetric stretching mode absorption at 2960 cm^{−1}, and a deformation mode at 1430 cm^{−1}.

Raman active modes for graphite and diamond produce peaks at 1575 and 1330 cm^{−1}, respectively. A subsidiary peak found at around 1350 cm^{−1} is attributed to *a*-C. The corresponding vibration mode is active for crystallites of finite size and its intensity varies inversely with the diameter of the crystals. The feature seen in the spectra of our films at 1352 cm^{−1} is identified to be *a*-C.

The 1167 cm^{−1} line seen in spectra of *a*-C/diamond films is also attributed to this Raman active mode of microcrystalline or amorphous diamond. Nemanich *et al.*²² observed a strong Raman peak at ~1140 cm^{−1} and deduced that this line was caused by microcrystalline diamond regions. They further stated that, by comparing wurtzite diamond with the frequencies for SiC, the most intense Raman peak characteristic of microcrystalline diamond would be expected to occur at ~1175 cm^{−1}.

Figure 4 shows the variation of *a*-C/diamond films deposited at approximately the same dc self bias, but with a varying CH₄:Ar ratio. Again, there is no correlation between the CH₄ content and the relative H content incor-

porated into the film during its growth. The IR peak around 3300 cm^{-1} , indicates triple bonded C—H which dominates the spectra appearing in Fig. 4, as seen in the case of Fig. 3. This suggests that in the α -C/diamond films deposited by our system, the majority of the hydrogen in the films is triple bonded C—H carbyne hybridizations.

At low CH_4 concentrations, the relative number of hydrocarbon species present in the chamber is small and would lead to thinner α -C/diamond films. This is seen in films dc114 to dc117. As expected the films deposited with a higher CH_4 concentration, are thicker (dc118 and dc128). Considering the number of C—H species present in the chamber during deposition, the films deposited at higher CH_4 concentrations should have more H incorporated into them. This is not, however, the case for α -C/diamond films, since the film deposited at 8% CH_4 :Ar ratio (highest $\text{CH}_4\%$) has the lowest H content in the film (Table III).

The behavior of the optical band gap of α -C/diamond films can be better explained by using the subplantation model proposed by Lifshitz *et al.*¹⁰ In this model energetic C^+ ions impinge on the growing C surface and create a subsurface layer. In this subsurface layer it is increasingly favorable for sp^3 bonded C to form and diamond crystallization to occur. The more energetic the ions, the better suited they are to form a metastable diamond phase and this is perhaps what the initial increase in the optical band gap reflects. At around -265 V an optimum condition is reached and a band gap of 4 eV is recorded. As the energy of the C^+ ions further increase, the model suggests that the ionized species have sufficient energy to amorphize the growing film. This then should result in a drop in the optical band gap of the material. This drop in band gap is seen in our results with increasing dc bias. An interesting result is that the peak in the optical band gap occurs in a dc bias window. This corresponds to the prediction of an optimal energy window for C ions to form diamond crystals in ion beam deposited films. It should be noted that our system is not an UHV ion beam system, but rather a plasma CVD system with ion acceleration across the sheath space. Hence the dc self-bias voltage is not a direct measure of ion energy due to the much higher pressure of the system. However, the ion energies from the theoretical calculations of Lifshitz *et al.* suggest that an optimum energy for C^+ ions to nucleate as diamond is $50\text{--}100\text{ eV}$. With the particular conditions of pressure and temperature used in our experiments, it is possible that the equivalent C^+ ion energy range is obtained at the substrate with dc bias voltages around -265 V . The theory that at high dc biases the film amorphizes the surface is reinforced by the increase in the refractive index and the compressive stress in the films.^{8,23} Amorphization can be thought of as the compaction of the deposited film due to the impact of high energy ions. Therefore, the rise seen in the refractive index and the increase in compressive stress in the α -C/diamond film, fits in well with the subplantation model proposed by Lifshitz *et al.*

CONCLUSIONS

The optical properties of α -C/diamond films deposited at room temperature from a CH_4/Ar plasma have been examined in the IR-to-UV range. The results show that the hydrogen in the films is predominantly bonded to $sp^1\text{ C}$. The optical band gap of the films is not directly related to the hydrogen content, though the films with the highest optical band gaps tend to have a relatively low hydrogen content. The major parameter which controls the optical band gap is the dc self-bias voltage developed during deposition. The existence of a dc bias window which results in the highest optical band gap is in accordance with the theory of Lifshitz *et al.* which postulates the existence of an optimum energy window for C ions to crystallize as diamond in films deposited on low temperature substrates.

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