

Unhydrogenated diamondlike carbon films prepared by dc plasma chemical vapor deposition at room temperature

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Unhydrogenated diamond-like carbon films prepared by dc plasma chemical vapor deposition at room temperature

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Unhydrogenated diamond-like carbon films were prepared at room temperature by a simple dc plasma chemical vapor deposition system with a low overall power consumption. A gaseous mixture of methane and argon (1:9) was used as a material gas with the intent of bombarding the growing film with Ar^+ ions. The bombardment of the depositing species with Ar^+ ions present in the plasma leads to (i) removal of hydrogen from the carbon atoms and (ii) a preferential resputtering of weakly bonded graphite precursors from the film surface giving rise to diamond-like properties of the films. The progressive thermal annealing of the films induces graphitization, and promotes growth of the crystallites at higher anneal temperatures (≥ 500 °C)

Thin films of diamond-like carbon (DLC) exhibit very interesting properties such as large thermal conductivity, high hardness, chemical inertness, electrical insulation, and optical transparency. These characteristics make DLC films highly suitable for coating material in microelectronics as well as in mechanical applications. Recent reviews focus very well on the properties and applications of DLC films.^{1,2} Diamond-like carbon consists of either pure amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) which can contain up to 30 at. % of hydrogen bonded in the amorphous carbon matrix. Unlike hydrogenated diamond-like materials the unhydrogenated DLC films were found^{3,4} moderately transparent in the visible and infrared wavelengths, and hence may have potential optical applications. The low-temperature deposition, required for microelectronics applications, of both hydrogenated and unhydrogenated DLC films has recently been reported using sputtering,⁵ laser evaporation,^{4,6} rf plasma decomposition,⁷ and electron cyclotron resonance chemical vapor deposition⁸ processes. The mechanical applications of DLC films demand thermal stability of these films at high temperatures. To the best of our knowledge, there are only two reports existing in literature on hightemperature annealing of amorphous carbon films.^{9,10}

The aim of the present letter is to report on the roomtemperature deposition of unhydrogenated DLC films achieved by using a simple and inexpensive dc plasma chemical vapor deposition (CVD) system with a low overall power consumption developed in our laboratory. The material gas was chosen to be a mixture of CH₄ and Ar(1:9) with the intent of bombarding the growing film with Ar⁺ ions. The structure of as-deposited and progressively annealed films was probed by Raman spectroscopy and the results are presented.

Figure 1 shows the schematics of the dc plasma CVD setup used to prepare DLC films. A high vacuum system with a glass belljar was used for this purpose. A pair of 15-cm-diam stainless-steel electrodes E with an interelectrode spacing of 2.5 cm was placed in the vacuum chamber C. Silicon substrates were placed on the lower grounded electrode. The upper power electrode was well insulated

from the stainless-steel mesh S (grounded) which was used to confine the plasma to the interelectrode space. The material gas (10% methane + 90% argon) was introduced into the chamber through gas inlet G. A dc plasma was created by applying a potential of 500 V to the upper electrode. The plasma current was 10 mA. No substrate heating was employed during the deposition process. Typical deposition conditions are shown in Table I.

The electrical resistivity of the films was measured in a planar geometry. The refractive index was measured using ellipsometry. The infrared absorption spectrum, in the range 400–4000 cm⁻¹, was obtained using a single-beam spectrophotometer (Bio-Rad FTS-40). Annealing of the samples was carried out in a quartz chamber at a pressure of ~10⁻⁵ Torr. A temperature controller was used to stabilize the temperature to ± 2 °C. The anneal duration was 30 min at a temperature of 200 °C and every 100 °C from 300 to 800 °C. The Raman spectra were obtained in a pseudo backscattering geometry using a Jobin Yvon Ramanor U-1000 double monochromator equipped with a photomultiplier and a photon counting system. The laser



FIG. 1. Schematic setup for dc plasma chemical vapor deposition system: (C) vacuum chamber, (E) stainless-steel electrodes, (S) stainless-steel mesh, (I) insulators, and (G) gas inlet.

TABLE I. Typical experimental conditions.

Substrate	Polished silicon
Material gas	10% methane + 90% argon
Flow rate	10 sccm
Pressure	200 mTorr
Voltage	500 V
Power	5 W
Temperature of deposition	Room temperature
Rate of deposition	~25 Å/min
Film thickness	~150 nm

light (488.0, 514.5, and 647.1 nm lines from Ar^+ and Kr^+ lasers) with a constant power level of nearly 150 mW was line focused onto the sample for all measurements.

The as-deposited films exhibited an electrical resistivity of $1.2 \times 10^6 \Omega$ cm and a refractive index of 2.1 (measured at 6328 Å). That the films did not contain hydrogen was confirmed by the absence of C-H absorption band near 2900 cm⁻¹ in the infrared absorption spectrum. The above-mentioned features and the Raman spectral profiles (shown in Fig. 2) of the as-deposited films strongly suggest the diamond-like nature of the films.⁵

The absence of hydrogen in the films can be explained in terms of the impact energy of the depositing and the bombarding ions on the substrate surface. Under the experimental conditions listed in Table I, the energy of these ions was calculated to be $\sim 20 \text{ eV}$.¹¹ The bombarding ions (Ar⁺ ions in our case) with this value of energy can cause a considerable cracking of the hydrocarbon species (depositing ions) leading to removal of hydrogen from the carbon atoms. Since the C—C bond strength ($\simeq 144 \text{ kcal/mole}$) is greater than that of C— H($\simeq 81 \text{ kcal/mol}$),¹² therefore only carbon atoms accumulate on the substrate while hydrogen atoms are sputtered off.

Raman spectrum of an as-deposited DLC film, ob-



FIG. 2. Raman spectra of a DLC film excited at different incident photon energies.

tained using the 514.5 nm line of Ar⁺ laser, is shown in Fig. 2 (middle spectrum). Note that the spectrum shows a close resemblance to those obtained for unhydrogenated DLC films by other workers,^{5,6} and exhibits a highfrequency peak at around 1530 cm⁻¹ and a low-frequency shoulder near 1300 cm⁻¹. The Raman band at about 970 cm⁻¹ correspond to the second-order line of the silicon substrate. Such a spectral profile has been attributed to the presence of a mixture of tetrahedral (sp^3) and trigonal (sp^2) C—C bonds present in the film.¹³ The highfrequency portion is assigned to a E_{2g} mode (G peak) in a graphitelike sp^2 -bonded carbon phase. The low-frequency portion is interpreted as scattering from sp^3 carbon plus a possible contribution of the graphite-like D peak.

The evidence that our films contain sp^3 -bonded carbon atoms comes from the energy dependence of the Raman spectra. Figure 2 shows the Raman spectra of an asdeposited DLC film excited at different energies of the probing radiation. With increasing photon energy, the position of the high-frequency band shifts from ~ 1485 (at 1.92 eV) to \sim 1540 cm⁻¹ (at 2.54 eV). The low-frequency band remains practically unchanged. Such a behavior has been explained in terms of a heterogeneous two-phase model involving sp^2 - and sp^3 -bonded carbon atoms.¹³ The differences in the electronic spectra of the two phases give rise to different dispersion curves for the Raman polarizability which in turn leads to a change in the relative weight of the two contributions to the Raman spectra obtained as a function of incident photon energy. Such a change in relative weight causes a frequency shift in the measured Raman spectrum.

As-deposited DLC films are known to consist of $\sim 2/3$ sp^3 - and $\sim 1/3$ sp^2 -bonded carbon.¹³ The presence of a predominant amount of sp^3 bonding in our DLC films is attributed to the concurrent argon-ion bombardment during the growth of the film. The ion bombardment causes a preferential resputtering of weakly bonded graphitic precursors from the film surface, and hence increases the relative concentration of sp^3 bonds. This mechanism can operate at very low ion energies since the bonding energy of graphitic precursors to the film surface is about 0.8 eV.¹⁴

We now discuss the structural changes which accompany the thermal annealing of as-deposited films. Figure 3 shows Raman spectra for the film as a function of anneal temperature T_A . As already mentioned the roomtemperature deposited film shows a graphite-like G peak $(sp^2$ -bonded carbon) near 1530 cm⁻¹ and another broad signal near 1300 cm⁻¹ attributed to scattering from sp^3 carbon plus disordered graphite-like D peak. Annealing of the film up to 400 °C results in a slight growth of the signal at 1300 cm⁻¹ accompanied by a small positive shift of the G peak. This observation indicates the beginning of growth of small crystallites and a rearrangement of carbon atoms, leading to reduced bond-angle disorder and/or stress in the film. After annealing at $T_A = 500$ °C, the Raman spectrum resembles that of a film consisting only of sp²-bonded carbon with a relatively sharp G peak at ~ 1600 cm⁻¹ and a broader D at ~1360 cm⁻¹. The G peak is assigned to scattering by graphitic optic zone centre photons (E_{2g})

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FIG. 3. Raman spectra of a DLC film, excited with 2.41 eV laser line, at various annealing temperatures.

mode) whereas the D peak is attributed to scattering by disorder activated optic zone edge phonons.¹⁰ At this stage, the film became very soft and poorly adhesive. This is clearly a manifestation of the graphite nature of the film. The electrical resistivity of the annealed film was found to be very low although no systematic measurement could be made due to the porous nature of the film.

Further annealing of the film at higher temperatures $(T_A > 500 \,^{\circ}\text{C})$ leads to an increase of *D*- to *G*-line intensity ratio, I(D)/I(G). This quantity is roughly proportional to the ratio of momentum nonconserving-to-conserving phonons which contribute to Raman spectrum. The *D* mode is Raman inactive for a carbon crystal of infinite size, but is activated for crystallites of finite dimensions which do not conserve momentum.¹⁵ Therefore, the increased I(D)/I(G) ratio can be understood in terms of the growth in number of small carbon crystallites. At low annealing temperatures ($T_A < 400 \,^{\circ}$ C), the existing crystallites contribute

little to the *D* line in the spectrum because of their small number. As the anneal temperature is increased the crystallites start growing in number and thus begin to contribute to the Raman spectrum, leading to an increasing value of I(D)/I(G). The observed decrease in linewidth of *D* and *G* peaks as T_A is increased also suggests the increasing dominance of crystallites and the removal of bond-angle disorder. A similar annealing behavior has been reported for evaporated⁹ and ion beam sputtered¹⁰ carbon thin films.

In conclusion, unhydrogenated carbon thin films prepared by dc plasma chemical vapor deposition exhibit diamond-like properties. The as-deposited films have been shown to consist of both sp^2 - and sp^3 -bonded carbon atoms. The formation of sp^3 bonding in the films is attributed to the concurrent Ar⁺-ion bombardment of the depositing species during growth of the films. High-temperature annealing (≥ 500 °C) of the films leads to growth of carbon crystallites. The crystallites are identified as having trigonal (sp^2) bonding because of the shift in Raman line positions towards graphite-like values.

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