Laser-Assisted Chemical Vapor Deposition of Graphite

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Photolysis of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride vapor using a beam from a KrF (248 nm) excimer laser focused onto a silicon substrate gives a carbon film. Analysis of the film by Auger electron spectroscopy gave three peaks at 268, 255, and 241 eV which confirms the graphitic nature of the carbon deposit. Raman spectroscopy in the reflectance mode gives a narrow band at 1577 cm^{-1}, similar to single crystal or highly ordered pyrolytic graphite; however, this band is accompanied by a weaker band at 1350 cm^{-1} which indicates there is some disorder in the graphitic structure. The use of the laser-assisted process allows the deposition of high-purity graphite films without heating the substrate, whereas the conventional thermal process requires deposition temperatures of 800 °C and annealing at 2000 °C to obtain a similar quality film.

Introduction

Vacuum processing of polymeric materials is a viable and clean alternative to solution processing.[1] Polymeric forms of carbon are of great interest in materials science for use as heat sinks, conducting polymers, protective coatings, lubricants, etc. However the lack of solubility of carbon for conventional solvent processing makes gas phase deposition an attractive method for the preparation of carbon-coated materials. Polymeric forms of carbon such as amorphous carbon, graphite, diamond-like carbon, and diamond all differ in the nature of chemical bonding between carbon atoms which leads to quite different chemical and physical properties for these materials. A number of elegant thermal methods have been developed for the selective preparation of these different forms of carbon.

Diamond and diamond-like carbon films can be prepared by high temperature–high pressure and low pressure–high temperature methods.[2] The low-pressure methods typically require heating the substrate to the temperature range 650–1200 °C. Graphite films can be prepared at temperatures above 2000 °C from a number of polymeric and monomeric precursors.[3–7] Graphite is thermodynamically more stable than diamond, and thus it might be expected to be readily formed from thermal decomposition of an organic molecule. However while many organic precursors can thermally decompose to carbonaceous material, selective formation of diamond or graphite from an organic precursor is quite rare.

In the design of a new process to prepare carbon films, light may be used in place of heat to overcome the very high temperatures that are required for thermal decomposition of an organic precursor. Lowering the temperature at which the organic precursor decomposes may permit more selectivity for the reactive intermediate to form polymeric carbon. We have recently reported a photochemical method for preparing carbon films, which contain diamond, from aliphatic carboxylic acid precursors.[8] In this paper we report the laser-assisted chemical vapor deposition (LCVD) of high-purity graphite from a monomeric, organic precursor under conditions of low pressure and low temperature.

Experimental Section

Naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (NTAD) was obtained from Aldrich Chemical Co. and used as received. The deposition cell for these experiments is shown in Figure 1. The vapor of the organic precursor and argon buffer gas were passed over a silicon substrate that could be resistively heated from 20 to 400 °C. Typically the total pressure in the deposition cell was 1–5 Torr, and the substrate was at ambient temperature or heated to about 150 °C. A KrF (λ = 248 nm) excimer laser (Lambda-Physik, EMG 101E) operating at 15 Hz was focused onto the surface of the silicon substrate with a 100 mm focal length cylindrical lens. The laser fluence was estimated from the spot size on the silicon substrate to be 100–300 mJ cm^{-2} per pulse. The vacuum cell was pumped by either a 4 in. oil vapor diffusion pump or a 14 L s^{-1} mechanical pump. The argon carrier gas was passed over a reservoir at 25 °C containing NTAD, and the mixture was admitted to the cell via a molecular leak valve to give a total pressure of 2 Torr in the cell. The cell was operated in a flow mode to provide a constant supply of

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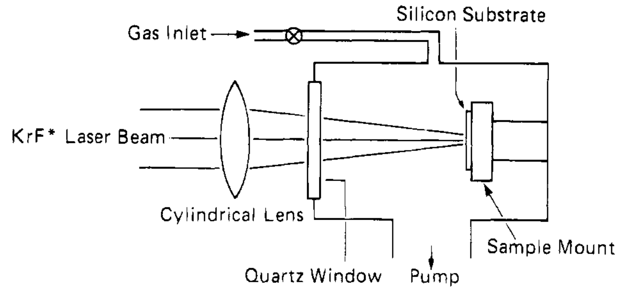

Figure 1. Chamber used for preparing the LCVD films.

the precursor to the photolysis region of the cell. No deposition occurred on the quartz window during the process. A typical experiment would last 0.5 h, after which the silicon substrate was removed from the vacuum cell. The deposits obtained with the focused laser are predominantly confined to the laser spot size, i.e., 1–3 mm × 10 mm. Some "spray-out" is noted outside the laser spot. The deposits were gray in appearance and approximately 1 μm thick. Larger deposits, 10 mm × 10 mm × 1 μm could be obtained with an unfocused laser.

The deposits were analyzed by both Auger electron spectroscopy (AES) and Raman spectroscopy. The Raman spectra were measured by Instruments, S. A., Edison, NJ. The AES analysis was performed in a separate vacuum chamber with typical background pressures of 5×10^{-9} Torr. A Perkin-Elmer Model C15–155 single-pass cylindrical mirror analyzer (CMA) with a beam spot size of 800 μm was used for the AES analysis. The output of the CMA was sent to an IBM PC for storage and analysis. The Auger specta were typically collected using a primary beam energy of 2 kV and a filament emission current of 0.5 mA. The emission intensity was kept low to minimize damaging (reconstructing) the surface. The samples were typically cleaned ultrasonically prior to introduction into the UHV chamber. After insertion to the system, the samples were allowed to degas to remove any physisorbed material from the surface before analysis. The samples could also be cleaned with low-energy (400 eV) Ar^+ ions and reanalyzed.

Results

The initial study of LCVD of carbon films involved using many organic precursors that included ketones, carboxylic acids, esters, alkyl halides, nitriles, amides, and aromatic compounds. The results from this study revealed that some precursors gave no deposit, others gave impure carbonaceous material (tar), and others gave carbon deposits. The nature of these carbon deposits was precursor dependent and could be disordered carbon, disordered carbon mixed with diamond, or graphite. Table 1 shows a partial list of the precursors studied and the nature of the deposited material. There is no strong evidence for a relationship between the structure of the precursor and the nature of the deposit. Thus while disordered carbon was obtained from CH_2R_2 when R = Br, tar was obtained from R = CN or $CONH_2$, and disordered carbon mixed with diamond was obtained from R = CO_2H. Similar results were obtained from the CH_3R series. While some carboxylic acid derivatives (CH_3CO_2H and $CH_2(CO_2H)_2$)) gave diamond with disordered carbon others did not. Aromatic carboxylic acid derivatives gave mainly disordered carbon with, in some cases small amounts of diamond. However from these studies it was found that LCVD using naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (NTAD) as the organic precursor consistantly resulted in the formation of relatively high-purity graphite. The graphite films were analyzed by Auger electron spectroscopy (AES) and reflectance Raman spectroscopy. The identification of the atomic composition and nature of the bonding of the deposited film is obtained from AES. The AES of a graphite deposit obtained from LCVD of NTAD is shown in Figure 2, along with the literature spectra of diamond, single-crystal graphite and amorphous carbon. The peaks have been labeled A_n and are listed with the literature values for amorphous carbon and diamond in Table 2. The AES for carbon corresponds to the KLL group of transitions in which the L states are the 2s and 2p valence states. The type of carbon bonding, sp^2 or sp^3, leads to distinctive line shapes of the derivative mode spectra. Thus graphite, which is all sp^2 carbon, gives three peaks, diamond (sp^3 carbon) gives four peaks, and amorphous carbon gives two peaks.[9,10]

While AES identifies the film as graphite, the structure of the sp^2 carbon film is better characterized by Raman spectroscopy in the reflectance mode. Figure 3 shows the Raman spectra of the LCVD graphite deposit, disordered carbon, natural diamond, a graphite deposit from a thermal process, and single-crystal graphite. The LCVD graphite deposit shows two bands at 1360 and 1577 cm^{-1}, the latter band being much more intense, whereas the disordered carbon film shows two broader peaks at 1354 and 1593 cm^{-1} of approximately equal intensity and natural diamond shows one band at 1333 cm^{-1}. Clearly the Raman spectrum of the LCVD graphite film shows no resemblance to diamond which is exclusively sp^3 carbon.[11,12] Also the LCVD graphite film is quite different from the disordered carbon film which gives much broader bands. There many types of disordered carbon: glassy carbon gives two Raman bands at 1343 and 1591 cm^{-1}; diamond-like carbon has a very broad band from 1100 to 1600 cm^{-1} centered at 1555 cm^{-1} with a shoulder at about 1350 cm^{-1}; coke gives two bands at 1357 and 1586 cm^{-1}; and charcoal has two bands at 1360 and 1584 cm^{-1}.[12] The band at around 1350 cm^{-1} is commonly known as the D band and the band at around 1580 cm^{-1} the G band. In the forms of disordered carbon described above the D band is always more intense than the G band, and both bands are broad. Single-crystal (natural) graphite and highly ordered pyrolytic graphite (HOPG) have sharp Raman bands at 1580 and 1576 cm^{-1} respectively, that are assigned to the E_{2g} C–C stretching mode.[11,12] The LCVD graphite film shown in Figure 3a shows one intense sharp band at 1577 cm^{-1} similar to the HOPG band and a weaker band at 1350 cm^{-1}, indicating some disorder.

Discussion

Pyrolytic methods for the preparation of graphite films typically requires initial pyrolysis of the precursor

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Table 1. Nature of Deposited Material Obtained by LCVD from Various Organic Precursors[a]

CH_2Br_2	disordered carbon	$CH_2(CN)_2$	tar
CH_3I	disordered carbon	$CH_2(CONH_2)_2$	tar
CH_3Br	disordered carbon/no deposit	phthalic anhydride	disordered carbon
diazo Meldrum's acid	disordered carbon	pyromellitic dianhydride	disordered carbon
CH_3CO_2H	disordered carbon/diamond	NTAD	graphite
$CH_2(CO_2H)_2$	disordered carbon/diamond		

[a] All films analyzed by AES and Raman spectroscopy.

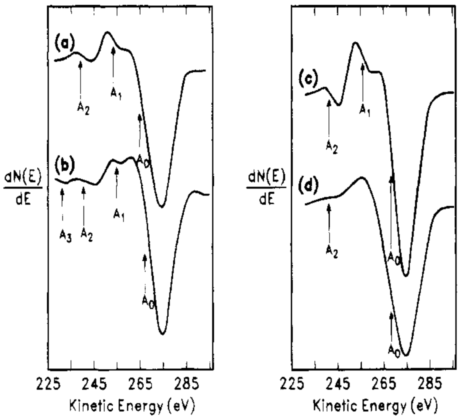


Figure 2. Auger electron spectra: (a) LCVD graphite film obtained using naphthalene-1,4,5,8-tetracarboxylic acid dianhydride precursor; (b) natural diamond; (c) graphite (after ref 10); (d) amorphous carbon (after ref 10).

Table 2. Auger Binding Energies (electronvolts)

	peak energy			
	A_0	A_1	A_2	A_3
graphite[a]	268	255	241	
natural diamond[b]	268	256	240	230
amorphous carbon[b]	268		243	

[a] This work (identical values were obtained for graphite in ref 10). [b] Reference 10.

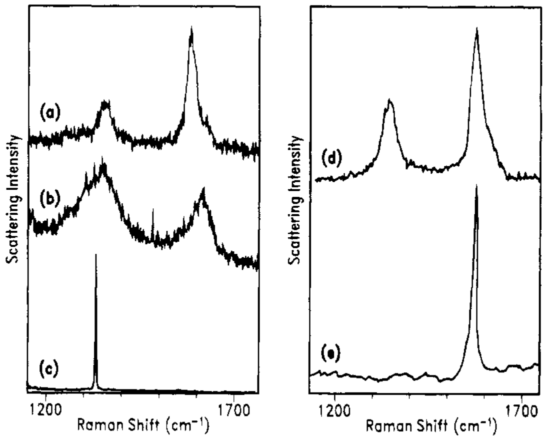
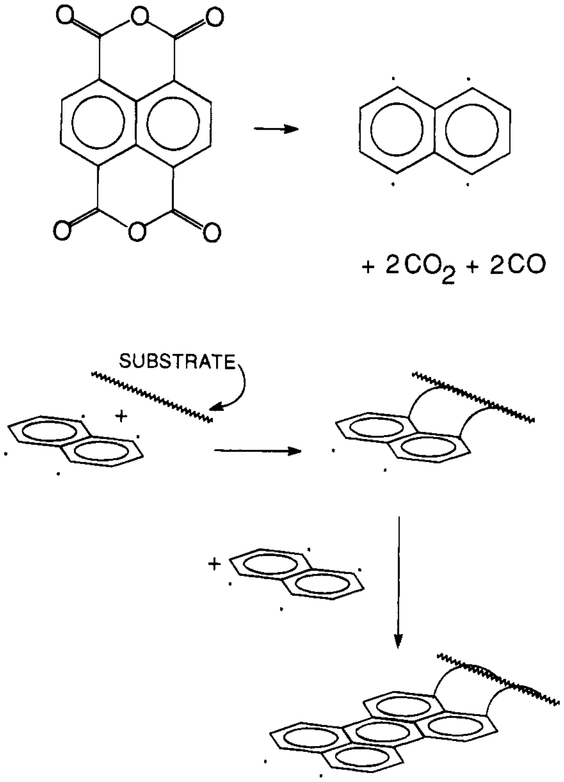


Figure 3. Reflectance Raman spectra: (a) LCVD graphite film obtained using naphthalene-1,4,5,8-tetracarboxylic acid dianhydride precursor; (b) disordered carbon; (c) natural diamond; (d) graphite film obtained from heating benzene to 850 °C and annealing at 2000 °C for 1 h (after ref 7); (e) single-crystal graphite (after ref 11).

Scheme 1. Mechanism for Formation of Perinaphthalene Units on Substrate



at temperatures of 700–900 °C to form the graphitic film followed by a second bake (anneal) at temperatures of 2000–2600 °C to remove disordered carbon. The films prepared by LCVD of NATD require no heating of the substrate, and the Raman spectrum shows only a minor component of the disordered carbon. On the basis of the intensities of the D and G bands, the LCVD film obtained from photolysis of NATD (Figure 3a) contains less disordered carbon than the film prepared from pyrolysis of benzene at 850 °C followed by an anneal at 2000 °C for 1 h (Figure 3d).[7] Thus the advantage of the laser-assisted method is the lower temperature required for processing. While it may be argued that the laser pulse will heat the substrate, there is no apparent surface damage. It is estimated from the fluences required for the deposition reaction that the substrate may experience a transient temperature rise of approximately 200 °C which is well below the temperatures used in the pyrolytic processes.

The mechanism we propose for the graphite film formation by the LCVD process involves a decarboxylation and decarbonylation reaction to give 1,4,5,8-tetradehydronaphthalene ($C_{10}H_4$), which reacts with the surface of the substrate (Scheme 1). This photochemical extrusion of CO_2 and CO is similar to the previously reported studies on the photolysis of phthalic anhydride which is known to give benzyne upon photolysis in N_2 matrices at cryogenic temperatures.[13] The graphite film is then built by further incorporation of $C_{10}H_4$ to the layer attached to the substrate and also by dehydrogenation of the resultant poly(perinaphthalene) units by hydrogen abstraction reactions from the free radical intermediates, e.g., $C_{10}H_4 \rightarrow C_{10}H_5 \rightarrow\rightarrow C_{10}H_8$. Thus

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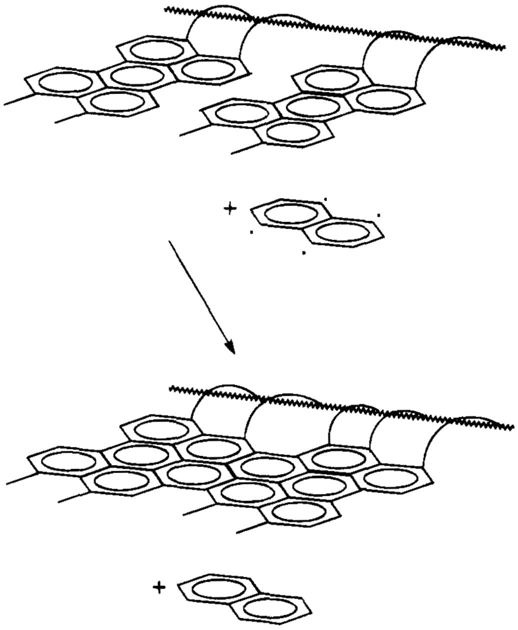
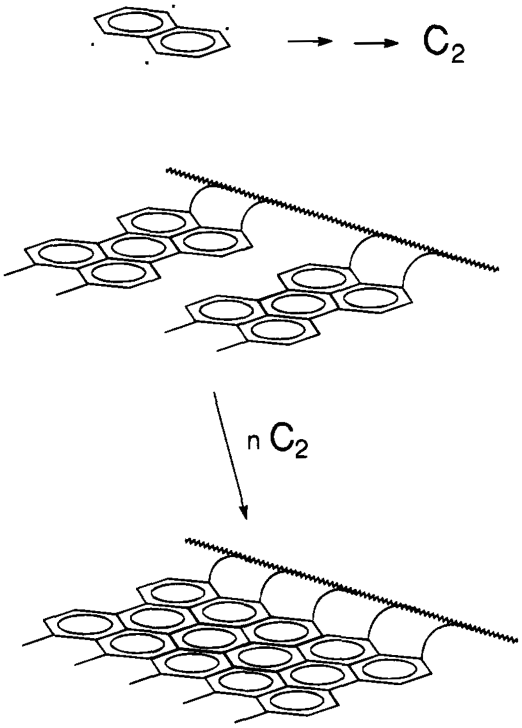
Scheme 2. Mechanism for Graphite Formation by Dehydrogenation with $C_{10}H_4$



the final products are the graphite film or volatile naphthalene derivatives.[14] The mechanism for this part of the process is similar to that previously proposed for a thermal process for producing a carbon film using perylene-3,4,9,10-tetracarboxylic anhydride as a precursor.[4] Direct cycloaddition of two adjacent perinaphthalene units by an in-phase dehydrogenation would be expected to give a four-membered ring which is expected to be unstable. However adjacent perinaphthalene attached to the surface may react by an out-of-phase dehydrogenation analogous to a [4+2] cycloaddition reaction (Scheme 2). Alternatively we speculate that two adjacent units may be coupled by carbon homologs smaller than naphthalene (C_{10}). For example, the route in Scheme 3 shows two in-phase units coupling by reaction with C_2. NTAD may be a precursor for C_2. It is known that prolonged photolysis of benzyne, a species that is produced from photolysis of phthalic anhydride, gives C_2 in an Ar matrix.[15] Thus an analogous reaction from laser photolysis of NATD could also generate C_2 for this reaction.

Scheme 3. Mechanism for Graphite Formation by Dehydrogenation with C_2



The main advantage with using light rather than heat for the deposition reaction is that the photochemical method appears to be more selective and gives pure graphite films at lower temperatures. Also, the use of a focused laser beam has the potential for patterning the graphite deposit onto the substrate by a direct-write method or through a mask by contact lithography.

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